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PREPARATION OF PITCH - WATER SLURRY.

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EXECUTIVE COMMENTS

In January 1987, this study was undertaken to evaluate a wide range of surfactants for the preparation of pitch-water slurries as feedstocks for entrained bed gasification. During the course of the contract, a number of anionic and non-ionic surfactants were evaluated. Two different hydrocracked pitches were utilized during the course of the study due to the limited supply of the CANMET material. While physical characteristics of the two materials differed somewhat, the goals outlined in the contract work statement were successfully achieved.

This study uncovered a number of interesting observations about the dispersive properties of the various surfactants when they are used in combination with hydrocracked pitches. In general, the lignosulfonate class of surfactants were found to be the most effective in the preparation of both the CANMET hydrocracked pitch and the PETRO-CANADA hydrocracked pitch. From a practical perspective, this group of surfactants are particularly attractive as they are readily available - they are a by-product of the pulp and paper industry - and they are relatively inexpensive.

While further evaluation will be required before this technology is adopted by industry, this study has demonstrated the feasibility of preparing aqueous slurries of petrochemical wastes. This may in turn, enhance the use of such materials as viable energy sources.

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SUMMARY

An investigation of the effects of several commercial surfactants on the stability and rheology of aqueous slurries of CANMET hydrocracked pitch and PETRO-CANADA hydrocracked pitch has been carried out. Additionally, limited studies of the effects of varying pitch concentration and particle size distribution (PSD) were also conducted. A simple rod penetration test, performed after the slurries had stood undisturbed for one week, yielded a parameter (A_{adj}) that was very sensitive to the nature and concentration of the surfactants examined in this work. Values of A_{adj}, obtained as a function of surfactant concentration, permitted the definition of a limited range of concentrations in which an optimum surfactant concentration is likely to be found. On this basis, the most effective surfactant will yield the lowest optimum surfactant concentration range.

In general, anionic surfactants were more effective at dispersing either pitch than nonionic surfactants. The concentration of surfactant required to achieve a given degree of dispersal more than doubled when the pitch concentration was increased from 50 wt% to 60 wt%. The practical maximum concentration of PETRO-CANADA hydrocracked pitch that can be incorporated into a slurry while maintaining optimum slurry behavior was established as 60 wt%. The effect of varying the PSD was not immediately clear from this work. However, in some cases the amount of surfactant required to yield a given degree of dispersion increased as the average particle size was reduced.

The rheological properties of the aqueous pitch slurries mentioned above were measured using a Brookfield viscometer. This work indicated that surfactants could dramatically reduce the viscosities of aqueous pitch slurries. However, there was no apparent correlation between slurry rheology and static stability. Moreover, there was no obvious relationship between the rheology of a slurry and the value of A_{adj} obtained from it.

Attempts were made to measure the contact angles of various liquids on the pitch powder by wetting rate measurements and application of the Washburn-Rideal equation to the data obtained from such measurements. This method required that a series of wetting rate measurements be performed using a homologous series of n-alkanes. Unfortunately, the pitch was soluble in these liquids. This would seriously compromise the validity of the Washburn-Rideal equation. Thus, it was not possible to complete these experiments.

Finally, intense ultrasound was evaluated as a method for dispersing the PETRO-CANADA hydrocracked pitch. On the basis of the results obtained in this work, it is highly unlikely that intense ultrasound, as it was applied in this work, will be an effective means for pitch dispersal.

Résumé

Ce rapport présente le compte-rendu des effets de plusieurs agents tensioactifs commerciaux sur la stabilité et la rhéologie de suspensions aqueuses de lignite noir hydrocraqué de CANMET et de PETRO-CANADA. De plus, quelques études partielles des effets du changement de concentration et de distribution de la grosseur des particules du lignite noir sont aussi décrites. Un simple test de pénétration d'une tige dans les suspensions, après que celles-ci aient reposé pendant une semaine, a produit un paramètre (A_{adj}) très sensible à la nature et à la concentration des agents tensioactifs. Les valeurs d'A_{adj}, obtenues en fonction de la concentration des agents tensioactifs, permettent de définir les limites d'une échelle de concentration optimale. A partir de cela, l'agent tensioactif avec la plus faible concentration optimale est considéré comme le plus efficace.

En général, notre étude montre que les agents tensioactifs anioniques sont plus efficaces pour disperser les deux types de lignite noir que les agents tensioactifs non-ioniques. Il est à noter que la concentration d'agent tensioactif requise pour disperser les particules doit être plus que doublée lorsque la concentration du lignite noir augmente de 50% (p/p) à 60% (p/p). La concentration du lignite noir hydrocraqué de PETRO-CANADA requise pour maintenir les propriétés optimales de suspension a été établie à 60% (p/p). Notre étude n'a pu clairement démontrer l'effet du changement de la distribution de grosseur des particules. Mais, dans certains cas, il est apparu que la quantité

d'agent tensioactif requise pour atteindre une dispersion donnée est inversement proportionelle à la grosseur des particules.

Les propriétés rhéologiques des suspensions aqueuses du lignite noir ont été mesurées à l'aide d'un viscomètre Brookfield. Ce travail indique que les agents tensioactifs peuvent réduire dramatiquement la viscosité des solutions aqueuses de lignite noir. Cependant, il n'y a pas de corrélation apparente entre la rhéologie des suspensions et leur stabilité statique. De plus, il n'y a pas de rapport évident entre la rhéologie d'une suspension et sa valeur d'A_{adj}.

On a tenté de mesurer les angles de contact de plusieurs liquides sur la poudre de lignite noir par mesure du taux de mouillage suivie de l'application de l'équation de Washburn-Rideal. Cette méthode implique que des mesures du taux de mouillage soient faites pour une série homologue de n-alcanes. Malencontreusement, le lignite noir est soluble dans ces liquides. Ceci compromet sérieusement la validité des données à partir de l'équation de Washburn-Rideal. Ces expériences n'ont donc pu être complétées.

Finalement, la méthode d'application d'ultrasons intenses pour disperser le lignite noir hydrocraqué de PETRO-CANADA a été évaluée. A partir des résultats obtenus pour ce travail, il est très peu probable que les ultrasons intenses, tel qu'utilisé pour ce projet, soient efficaces pour disperser le lignite noir.

CONCLUSIONS

The simple penetration test employed in this work provides a means of assessing the state of a slurry sediment. The adjusted penetration area (A_{adj}) derived from this test is related to the average work required to penetrate a unit length of the sediment. A_{adj} can be used to establish a range of surfactant concentrations in which an optimum concentration is likely to be found.

The optimum surfactant concentration provides a slurry which possesses the optimum combination of fluidity and stability. Slurries which contain less than the optimum concentration are very stable. However, such slurries are also highly flocculated and exhibit excessively high viscosities. Slurries which contain more than the optimum concentration are very fluid; but these slurries are also highly unstable.

Slurries that were prepared from the two types of pitch examined in this work, exhibited somewhat different behavior. Frequently, with slurries that were prepared with CANMET hydrocracked slurries, the transition from a highly flocculated, and therefore excessively viscous system, to one that was very fluid, and extremely unstable, occurred over a very small of range concentrations. In some cases this range was less than 0.10 wt%. This is undesirable since very small changes in slurry composition can result a significant deterioration of the slurry properties. The use of a stabilizing agent such as guar gum would reduce this problem by inhibiting sedimentation in deflocculated slurries; thereby widening the transition range.

On the other hand, the above mentioned transition occurred over a relatively wide range of surfactant concentrations when slurries were prepared from PETRO-CANADA hydrocracked pitch. Furthermore, the range of surfactant concentrations that yielded optimum slurry behavior are also quite wide (>1 wt%). Thus, if the surfactant concentration is well within the optimum range, the slurry will be much less susceptible to small changes of surfactant concentration than would be the case with slurries containing PETRO-CANADA hydrocracked pitch. The differences in the behavior exhibited by slurries containing CANMET hydrocracked and those containing PETRO-CANADA hydrocracked pitch are probably attributable to differing particle size distributions and differences in chemical composition.

In general the anionic surfactants were more effective than the nonionic surfactants employed in this work; since lower concentrations of the anionic surfactants were required to achieve a given degree of pitch dispersion than were required by the nonionic surfactants. The lignosulphonates (LIGNOSOL XD, LIGNOSOL TSD, MARASPERSE CBX-2 and MARASPERSE CBOS-3) were the most effective surfactants for preparing slurries of CANMET hydrocracked pitch. The most effective surfactants for the preparation of PETRO-CANADA hydrocracked pitch slurries were, in order of effectiveness: LIGNOSOL XD, LIGNOSOL TSD, LIGNOSOL BD and the anionic surfactant LOMAR D.

Significantly higher concentrations of surfactants were required to achieve a given degree of dispersion in slurries containing 60 wt% -200 mesh CANMET hydrocracked pitch than were required by slurries containing 50 wt% -200 mesh CANMET hydrocracked pitch. A more thorough study of the effect of PETRO-CANADA hydrocracked pitch concentration on the minimum concentration of surfactant (LIGNOSOL XD) required to yield optimum slurry behavior (the ORLL) gave similar results. The data obtained in this study allowed the development of a simple correlation between pitch concentration and the ORLL. According to this correlation, slurries could exhibit optimum behavior only if they contained less than approximately 62 wt%. In fact, it was not possible to prepare slurries of PETRO-CANADA hydrocracked pitch with pitch concentrations in excess of 62 wt% or fluid slurries with pitch concentrations in excess of 60 wt%. Thus, 60 wt% represents the practical maximum concentration of PETRO-CANADA hydrocracked pitch that can be employed in an aqueous slurry.

In some cases higher concentrations of surfactant were required to achieve a given degree of dispersal by slurries containing -325 mesh CANMET hydrocracked pitch than was the case for slurries that contained -200 mesh CANMET hydrocracked pitch. However, more data are required before the effect of varying particle size distribution can be definitively established.

The rheological data provided by the Brookfield viscometer indicated that surfactants can drastically reduce the viscosity of aqueous pitch slurries. These data also indicated that once the viscosity of a slurry reached a certain level (11-50 cP for CANMET hydrocracked pitch slurries, 150-500 cP for PETRO-CANADA hydrocracked pitch slurries) further additions of surfactant had little effect. Consequently, when viscosity reduction alone is considered, it is wasteful to employ a concentration of surfactant higher than that required to yield a viscosity in this range. In general this concentration increased substantially as the concentration of either type of pitch increased.

Most of the slurries containing the -325 mesh CANMET hydrocracked pitch exhibited pseudoplastic (shear thinning) behavior. On the other hand, many of the slurries containing -200 mesh CANMET hydrocracked pitch exhibited dilatant (shear thickening) behavior. On this basis, it would seem that the -325 mesh size fraction is more desirable than the -200 mesh size fraction. Most of the slurries prepared with PETRO-CANADA hydrocracked pitch exhibited dilatant behavior. The only exceptions were slurries containing more than 1.50 wt% LOMAR D and a few slurries prepared with PLURONIC F-108.

There seems to be little correlation between the stability of a slurry and its rheology as measured in the present study. Moreover, there does not seem to be a relationship between the value of A_{adj} obtained from a slurry and its rheology. However, more data are required before such relationships can be ruled out.

The pitch examined in this work showed a significant solubility in n-alkanes. Therefore the application of the Washburn-Rideal equation to the wetting rates obtained using these liquids is of dubious validity. However, it is necessary to employ such liquids if contact angles are to be obtained for surfactant solutions. Consequently, it was not possible to obtain values for the contact angles of the surfactant solutions on the pitch.

Finally, intense ultrasound was much less effective as a means for the dispersal of PETRO-CANADA hydrocracked pitch than was conventional mechanical mixing.

RECOMMENDATIONS

On the basis of the present work the following recommendations are made:

(1) Slurries containing PETRO-CANADA hydrocracked pitch should be prepared using one of the LIGNOSOL brand lignosulphonates or LOMAR D as the surfactant. LIGNOSOL XD is effective at the lowest concentration, while LOMAR D yields the most desirable rheology. Slurries that contain CANMET hydrocracked pitch can be prepared from any of the lignosulphonates investigated in this work or LOMAR D.

(2) The highest concentration of PETRO-CANADA hydrocracked pitch that should be employed for slurry production is 60 wt%.

(3) Slurries containing 60 wt% of PETRO-CANADA hydrocracked pitch should contain between 1.09 and 2.30 wt% of LIGNOSOL XD or between 2.00 and 3.00 wt% of LOMAR D for optimum slurry performance.

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1.0 INTRODUCTION

1.1 Objective

Materials such as oil sand coke and pitch are produced in large quantities as by products of commercial oil petroleum refining processes. Although these materials possess high carbon contents, the opportunities for their economic utilization are limited. Consequently, such materials are attractive feed stocks for processes, such as gasification, which depend on low cost feedstocks for their commercial viability.

High gasification conversions can be obtained in an entrained bed reactor. A slurry feeding system would increase the flexibility of this type of reactor, but the operation of such a system depends on the stability and pumpability of the feed slurry. Additives such as surfactants can be used to control these properties.

The goal of this study is the evaluation of a wide variety of commercial surfactants for slurry preparation. Additionally, an assessment will be made of any advantage of intense ultrasound as a mixing method over conventional mechanical mixing.

1.2 Introduction

Recently, slurries have been the subject of great interest; this is particularly true of slurry fuels. Slurries provide a means to treat solid materials as if they were fluids. Consequently, slurried materials can be transported and used almost as easily as true liquids.

It is usually desirable to obtain slurries with the highest concentration of suspended solids that is possible, as this increases transportation efficiency. The limit on the solids content of a given slurry is determined by a number of negative consequences of high solids content, eg. high viscosity. Modern slurry formulation involves the use of additives to achieve high solids content (up to 70% by wt.) while minimizing the negative effects. The selection of suitable additives is based on a consideration of surface properties and rheology. Therefore it is not surprising that such additives are usually surfactants. Accordingly, a brief consideration of surfactants and their role in slurry preparation is given below.

1.3 Surfactants

1.3.1 Introduction

Surfactants are some of the most important and useful chemicals produced by the chemical manufacturers. In addition to their familiar role in cleaning, they are also used in such diverse applications as: lubrication, pharmaceuticals, drilling muds and flotation agents. Surfactants have been studied for many years and they have been widely reviewed as a class of chemicals (2-10). However, the selection of a given surfactant for a particular purpose is still more a matter of art than of science.

Rosen (2) has defined a surfactant as a material, which when present at low concentration, adsorbs onto the interfaces of a system and significantly alters the interfacial free energy of those interfaces. The interfacial free energy is the minimum amount of work required to create an interface. The interfacial free energy per unit area is called the interfacial or surface tension. Frequently the term surface is reserved for an interface between a liquid or solid and a gas. In the present work, however, no distinction is made between surface and interface.

Surface molecules interact more strongly with molecules in the bulk than they do with the phase above it. Accordingly, surface molecules are at higher potential energies than molecules in the bulk material. Consequently, work is required to bring a molecule from the bulk to the surface.

All surfactants have an amphipathic molecular structure. This consists of a group with little affinity for the solvent liquid and a group which has a high affinity for the solvent. These groups are known as lyophobic and lyophilic groups respectively. However, since the systems usually considered involve aqueous solutions, the terms hydrophobic and hydrophilic will be used. The hydrophobic group on a surfactant molecule will distort the water structure when it is dissolved, this leads to an increase in the free energy of the system. Less work is thus required to bring a surfactant molecule to the surface than is required to do so for a water molecule, and surfactant molecules therefore tend to concentrate at the surface. Moreover, since less work is required to bring molecules (namely surfactant molecules) from the bulk to the surface, the surfactant reduces the work required to create a unit area of surface (or surface tension).

The presence of the hydrophilic group prevents the formation of a separate phase, since this would require its dehydration. Thus, the surfactant molecules are oriented with their hydrophilic group in the water and their hydrophobic group directed away from it. The structures of the hydrophobic and hydrophilic groups determine whether a given surfactant will be active in a particular system. The hydrophobic group is often a long hydrocarbon chain. The nature of the hydrophilic group varies widely and provides a method for classifying surfactants. On this basis, the four major classes of surfactants in water are:

(i) Anionic- the hydrophilic group bears a negative charge,

(ii) Cationic- the hydrophilic group bears a positive charge,

(iii) Zwitterionic- both positive and negative charges are present on the hydrophilic group,

(iv) Nonionic- the hydrophilic group does not bear any charge.

Only anionic, cationic and nonionic surfactants will be considered further since they are by far the most important of the four classes.

1.3.2 Anionic Surfactants

Anionic surfactants are the most widely used of the four surfactant classes (2). Therefore, they have been the subject of several monographs (4,5). Carboxylic acid salts are perhaps the most familiar anionic surfactants. Common soap has been produced from the sodium and potassium salts of straight chain fatty acids for centuries. To be effective in water, the fatty acid chains usually contain between ten and twenty carbon atoms. These soaps are sensitive to pH and ionic strength. They also form water insoluble compounds with divalent and trivalent metal ions.

The traditional source of the fatty acids used in such soaps has been tallow. The mixture of fatty acids obtained from coconut oil has a different distribution than those obtained from tallow. Soaps produced from coconut oil fatty acids have some resistance to electrolytes. Fatty acids can also be obtained from tall oil (a byproduct of paper manufacture). Tall oil contains roughly 50-70% fatty acids and 30-50% non linear rosin acids (2). Tall oil soaps are less expensive, more soluble in water and more resistant to divalent and trivalent metal ions than are tallow soaps.

Sulfonic acid salts are as widely used as carboxylates. These materials are not as easily prepared, since they require a sulphonation step.

Linear alkylbenzene sulfonates at one time were the most widely used industrial and household surfactants until environmental concerns reduced domestic consumption (4). They are composed of randomly distributed benzene rings along a linear alkyl chain containing about twelve carbons. These materials are highly water soluble and have excellent dispersing powers.

Lignosulfonates are produced as a by product of paper manufacture. These materials are produced in large amounts and are some of the most inexpensive surfactants available. They consist of sulfonated polymers with complex structures and molecular weights of about 1,000 to 20,000. These materials are very soluble in water and are excellent dispersing agents for carbon black (2).

Condensates of naphthalene sulfonic acid with formaldehyde are also widely used. They have similar properties to lignosulfonates and can be used as substitutes when lignosulfonates are incompatible with the desired use.

The surfactants described above represent only a few of the more commonly used anionic surfactants. The reader is directed to one of the aforementioned reviews for a more extensive description of these materials.

1.3.3 Cationic Surfactants

Cationic surfactants are used in only a small fraction of the applications found for anionic surfactants. Generally, these materials contain; long chain amine salts, diamines, polyamines and their salts, amine oxides or polyethoxylated long chain amines. Cationic surfactants are used as emulsifiers, adhesion promoters and in cosmetics. They are usually poor dispersing agents and are rarely used in slurry preparation (6).

1.3.4 Nonionic Surfactants

In terms of consumption, nonionic surfactants are surpassed only by anionic surfactants (2). Several monographs (7,8,9) have dealt specifically with nonionic surfactants. It is noteworthy that nonionic surfactants are resistant to polyvalent metal ions and high electrolyte concentrations.

An important group of nonionic surfactants are the polyoxyethylenated alkylphenols and alkylphenol ethoxylates. These materials are usually either p-nonylphenol, p-octylphenol, p-dodecylphenol or dinonylphenol. The length of the hydrophobic alkyl chain on the phenol or the hydrophilic polyoxyethylene chain can be varied. This allows the production of materials with widely varying solubilities in aqueous and non-aqueous systems. These substances are very stable chemically and are widely used as industrial detergents and emulsifiers. They are also excellent dispersing agents for carbon black (2).

Polyoxyethylenated - polyoxypropylenated glycols are simple copolymers of ethylene oxide and propylene oxide. Products with a wide variety of properties can be tailor made simply by varying the molecular weight and the relative amount of hydrophobic propylene oxide and hydrophilic etnylene oxide groups. For example, high molecular weight (about 30,000) products with a high ethylene oxide content (about 80%) are used as dispersants for pigments in paints (2).

Other types of nonionic surfactants can be produced by esterifying polyoxyethylene glycols with fatty acids or condensing them with diethanolamine. Since their structures and therefore their properties are so easily controlled, nonionic surfactants have been specifically produced for a staggering variety of uses. The substances considered above represent only a small, but important, fraction of the nonionic surfactants currently available. The reader is directed to one of the monograghs dealing with this subject for more information about nonionic surfactants of all kinds.

2.0 THEORETICAL ASPECTS OF SURFACTANTS IN SLURRY PREPARATION

2.1 Introduction

The major goal in slurry preparation is the dispersal of solid particles in a liquid medium. The role of surfactants in this process is considered in terms of three major steps. According to Parfitt (10), these are:

(i) wetting of a solid powder by a liquid,
(ii) breaking up of agglomerates and aggregates,
(iii) prevention of reaggregation.

Each of these steps is discussed in detail in the sections that follow.

2.2 Wetting And Contact Angles

2.2.1 Introduction

The contact angle is a very important property of the interface between two fluids (at least one of which is a liquid) and a solid. It originates from Young's 1805 treatment of the mechanical equilibrium of a drop resting on a plane solid under the influence of three surface tensions (see Fig. 2.1)

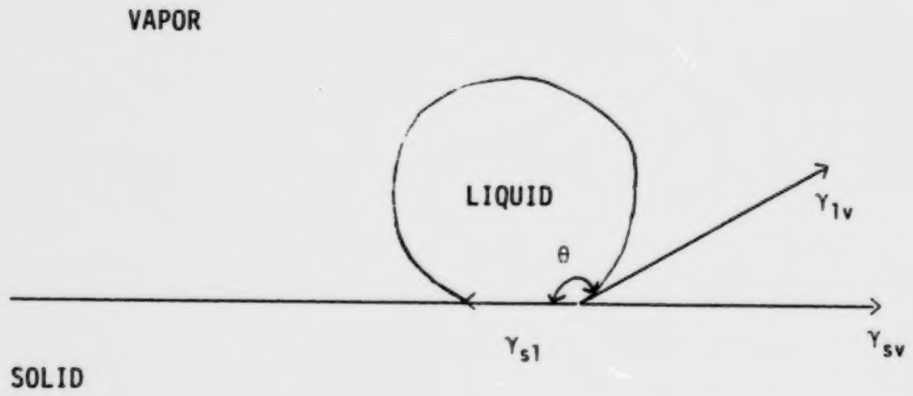

VAPOR
LIQUID
θ
γ_{lv}
γ_{sl}
γ_{sv}
SOLID

Figure 2.1 Contact angle of sessile drop.

Considering the force balance for the situation in fig. 2.1, one obtains:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \qquad [2.1]$$

On this basis, the reversible work of adhesion, W_a, is given by:

$$W_a = \gamma_s + \gamma_{lv} - \gamma_{sl} \qquad [2.2]$$

Where γ_s is the surface free energy of the solid-vacuum interface. W_a represents the work required to create a unit area of solid-vacuum and liquid-vapour interface from a unit area of solid-liquid interface. If the solid surface is coated with an adsorbed film of vapour equation [2.2] can be rearranged to give:

$$W_a = \gamma_{lv}(1 + \cos \theta) \qquad [2.3]$$

2.2.2 Wetting

All liquids wet all solid surfaces to some extent (ie. no liquid gives a value of 180° for θ on any solid). Generally a liquid is said to wet a solid if $\theta = 0°$ and does not wet a solid if $0 > 90°$.

In the case where θ 0° equation [2.1] does not hold and the imbalance of surface free energies is defined in terms of the spreading tension S as it is defined in equation [2.4].

$$S = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \qquad [2.4]$$

For spreading to be spontaneous, it must be accompanied by a decrease in free energy (ie $S > 0$).

The wetting of a powder is an important step in the preparation of any slurry. It is more useful to break this up into three distinct wetting processes. These are designated as adhesional wetting, spreading wetting and immersional wetting according to which physical process is operative. A discussion of each step follows below.

(i) Adhesional Wetting

A plane solid with an area of 1 m^2 is brought into contact with 1 m^2 of liquid surface to form 1 m^2 of solid-liquid interface. The work involved in this process ($W_{slv,a}$) is given in equation [2.5].

$$W_{slv,a} = \gamma_{sl} - (\gamma_{sv} + \gamma_{lv}) \qquad [2.5]$$

(Note $W_{slv,a} = -W_a$).

(ii) Immersional Wetting

When 1 m^2 of solid-vapour surface is immersed in a liquid, the work involved is:

$$W_{slv,i} = \gamma_{sl} - \gamma_{sv} \qquad [2.6]$$

(iii) Spreading Wetting

When a liquid drop spreads over a solid surface, equivalent areas of liquid-vapour and solid-liquid surface are formed from each unit area of solid-vapour surface that disappears. $W_{slv,s}$ gives the work of spreading wetting and is defined by equation [2.7].

$$W_{slv,s} = \gamma_{sl} - \gamma_{sv} \qquad [2.7]$$

These processes are easily visualized if the solid particles are considered to be cubes as shown in figure 2.2. If each side is 1 m, the energy changes that take place are:

(A) to (B) Adhesional Wetting

$$\begin{aligned} W_{slv,a} &= \gamma_{sl} - (\gamma_{sv} - \gamma_{lv}) \qquad [2.8] \\ &= -\gamma_{lv}(\cos\theta + 1) \end{aligned}$$

(B) to (C) Immersional Wetting

$$\begin{aligned} W_{slv,i} &= 4\gamma_{sl} - 4\gamma_{sv} \qquad [2.9] \\ &= -4\gamma_{lv}\cos\theta \end{aligned}$$

(C) to (D) Spreading Wetting

$$\begin{aligned} W_{slv,s} &= (\gamma_{sl} + \gamma_{lv}) - \gamma_{sv} \qquad [2.10] \\ &= -\gamma_{lv}(\cos\theta - 1) \end{aligned}$$

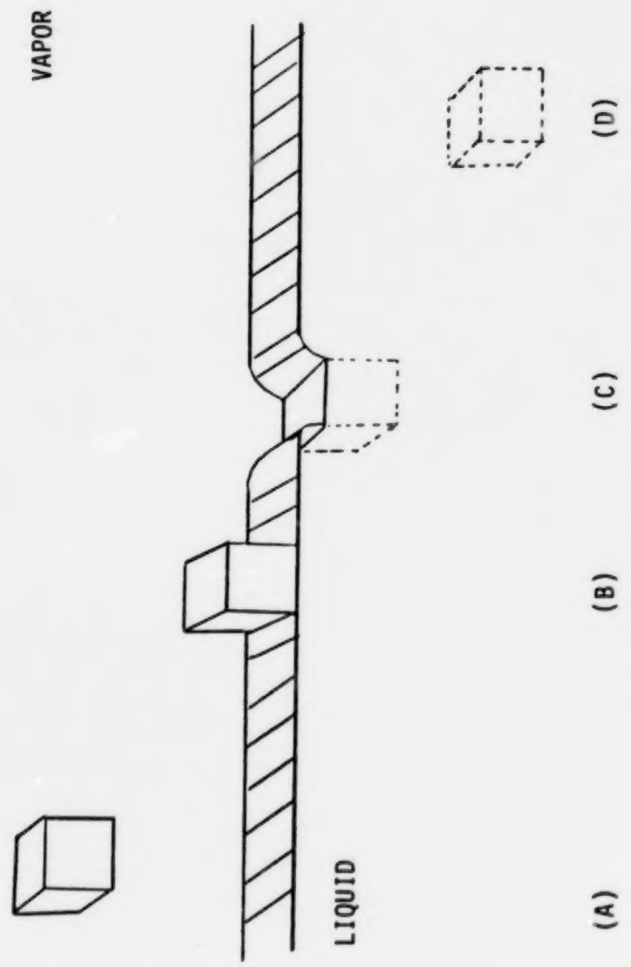

VAPOR
LIQUID
(A)
(B)
(C)
(D)

Figure 2.2 Stages in wetting.

The powder would wet spontaneously only if the work required (W_t) is negative. Thus, considering the three separate processes, the following conditions for θ are required for spontaneous wetting:

(i) adhesional wetting, $\theta < 180°$,
(ii) immersional wetting, $\theta < 90°$,
(iii) spreading wetting, $\theta = 0°$.

For the whole process W_t is given by the sum of the work required for each step.

$$\begin{aligned} W_t &= W_{slv,a} + W_{slv,i} + W_{slv,s} \\ &= -6\gamma_{lv}\cos\theta \end{aligned} \qquad [2.11]$$

Equation [2.11] implies that $\theta < 90°$ is sufficient for spontaneous wetting. However, since spreading wetting requires that $\theta = 0°$, this must be considered the primary criterion for spontaneous wetting of the powder. If this condition is not met then the powder would tend to float and work would be required to achieve spreading. For this reason, surfactants are used to ensure that θ is close to 0°.

2.2.3 Measurement Of Contact Angles

2.2.3.1 Introduction

Techniques for measuring contact angles have been the subject of several reviews (11,12). Frequently contact angles are measured by observing the profile of a sessile drop on a plane solid surface (13,14). This technique cannot be applied to the measurement of contact angles on powdered solids. Although observations have been made of sessile drops on the surface of a polished, compressed cake of the powder (15,16), there is some doubt as to whether the surface of such a cake is the same as that of the actual powder (12). Such cakes have also been found to be porous - allowing liquid to soak into the cake during measurement. This causes a large statistical scatter of the values obtained by this method (15).

2.2.3.2 The Washburn-Rideal Equation

The Washburn-Rideal equation describes the flow of a liquid through a capillary. This equation can be applied to a powder packed in tube if such a system is considered as a bundle of capillaries (13,17-22). If the effect of gravity is neglected and an empirical constant (K) (which accounts for the "tortuosity" of the powder bed) is introduced, the Washburn-Rideal equation has the form shown in equation [2.12].

$$h^2 = \frac{K \gamma_{lv}}{\eta} \cos \theta \ (t) \qquad [2.12]$$

Where h is the distance to which the liquid front moves in the time t and η is the viscosity of the medium.

Although some objection has been raised regarding the validity of equation [2.12] for finding contact angles (12), the discrepancies have generally been small (17-22). Thus, θ can be found from the slope of a plot of h^2 as a function of t (obtained by observing the rate at which a liquid wets a powder contained in a tube) if values of K, η and γ_{lv} are known. Values of η and γ_{lv} can be easily obtained. A value of K can be found provided that: the powder is uniformly and reproducibly packed, a constant particle size fraction is used, and the packing of the powder bed is not altered by wetting.

The determination of a value for K is considered to be one of the major drawbacks of the "Washburn-Rideal" technique (12). Frequently a liquid is chosen arbitrarily and assumed to give a contact angle of 0° on the solid (17,18,20). However, the possibility exists that this is not the case. Recently Rudoi and coworkers (18), have used Zisman's (23) critical surface tension concept to overcome this problem.

Zisman and coworkers (23) found that the dependence of θ on γ_{lv} for a a given series of liquids was given by:

$$\cos\theta = 1 - \text{constant}(\gamma_{lv} - \gamma_c) \qquad [2.13]$$

Where γ_c is the critical surface tension at which the contact angle becomes 0°. This value has been found to be primarily determined by properties of the solid and is only slightly dependent on the properties of the wetting liquid (24).

Rudoi et al (18) determined Kcos θ (assuming equation [2.12]) by measuring the wetting rates of quartz powder with a homologous series of n-alkanes. They found that Kcos θ initially increased linearly as the value of γ_{lv} decreased. Eventually a point was reached where Kcos θ remained constant even though γ_{lv} decrease. The value of γ_{lv} at this point was taken to be the critical surface tension. On this basis, liquids with surface tensions equal to or lower than the critical surface tension were assumed to give $\theta = 0°$. Thus, an unambiguous value of K can be found in this way. Since K is determined only by the powder, the value of K determined in this way is also valid for all liquids.

2.3 Breaking Of Agglomerates And Aggregates

After a solid is ground into a powder, the particles tend to adhere to each other forming clusters. Particles which are joined along their edges are held together by weak forces and require little energy to disperse. In fact, penetration of the liquid into the interparticle channels may generate forces which are sufficient to disperse the particles. Clusters such as these are frequently referred to as agglomerates.

Particle clusters in which the particles are joined along "crystal" faces are often called aggregates. The forces between particles in aggregates are much stronger than those in agglomerates. Thus, even high shear mixing may not be sufficient to disperse particles in aggregates. Consequently, a further comminution step may be required.

2.4 Prevention Of Reaggregation

2.4.1 Introduction

Particle aggregation determines the properties of slurries such as: static stability, flow properties and their eventual utility. Consequently, the control of particle reaggregation is perhaps the most important of the three steps mentioned in 2.1.

The magnitude of the forces between particles in a suspension determine whether particles remain individual units or join together to form secondary units such as agglomerates. The final state of the particles in the slurry depends on the eventual end use of the slurry. For example it may be desirable to maintain the particles as individual units so that the viscosity is kept as low as possible. Surface active agents allow some control over the state of the slurry by their influence on the various interparticle interactions.

2.4.2 Interparticle Forces

2.4.2.1 Introduction

There are three major types of interaction between suspended particles:

(i) Van der Waals interactions,

(ii) coulombic interactions,

(iii) steric interactions.

The particles in a suspension will remain dispersed if they are separated sufficiently for the repulsive forces to exceed the attractive forces. Each of the three interactions is briefly considered in the succeeding sections.

2.4.2.2 Van der Waals Interactions

The Van der Waals forces arise from the interactions between: dipoles, dipoles and induced dipoles, and instantaneous dipoles due to electronic motion within molecules. The latter two forces are always attractive. The Van der Waals interaction energy for a spherical particle, with radius a, in a vacuum is given by equation [2.14].

$$V_a = -\frac{Aa}{12H} \qquad [2.14]$$

Where A is the Hamaker constant and H << a is the distance between the particle surfaces. The Hamaker constant can be defined as shown in equation [2.15].

$$A = 0.75\pi^2 N\alpha^2 I \qquad [2.15]$$

Where α is the polarizability, N is the number density of atoms in the molecule and I is the ionization potential. Thus, large polarizabilities are a prerequisite for large values of A.

In a liquid medium A must be replaced by an "effective" Hamaker constant. If the ionization potentials of the medium and the molecules in the particle surface are not too different, the effective Hamaker constant is given by:

$$A_{12} = (A_{11}^{1/2} - A_{22}^{1/2})^2 \qquad [2.16]$$

Where A_{22} and A_{11} are the Hamaker constants for the dispersing medium and the particle respectively.

It can be shown (10) that the effect of an adsorbed surfactant layer (which may have Hamaker constant A_{33}) depends on the relative magnitudes of A_{11}, A_{22} and A_{33}. Normally $A_{11} > A_{22}$ (10) so that V_a is reduced if $A_{33} > A_{22}$ and increased if $A_{33} < A_{22}$.

2.4.2.3 Coulombic Interactions

The coulombic interaction between particles (V_e) is always repulsive. V_e depends on the size and shape of the particles, the distance between them, their surface potential Ψ_0, the ionic strength and dielectric constant ε of the medium. For a spherical particle of radius a, V_e is defined in equation [2.17].

$$V_e = \frac{\varepsilon a^2 \Psi_0^2}{H + 2a} \exp(-\kappa H) \qquad [2.17]$$

Where κ is the reciprocal electric double layer thickness. This can be influenced by the ionic strength as its magnitude is roughly proportional to the square root of the ionic strength.

Surfactants can influence V_e primarily by changing the surface potential of the particles. They are normally used at such low concentrations that even ionic surfactants have little effect on the ionic strength of the dispersing medium (24). However, the addition of concentrated electrolytes can greatly reduce the thickness of the double layer (24) which would reduce the effective range of the coulombic interactions accordingly.

2.4.4 Steric Interactions

Long chain surfactants can form thick adsorbed layers on suspended particles. Steric interactions arise as soon as these layers begin to overlap and interfere with each other. It is thought that there are two major contributions to the overall steric interaction energy.

The first contribution arises from the build up of segment concentration in the overlap zone. This leads to an increase in the local osmotic pressure and free energy. The chemical potential of the solvent is lower in the overlap region than it is in the rest of the adsorbed layer or the bulk liquid. Solvent molecules will tend to diffuse into the overlap zone from the bulk, tending to force the particles apart. Consequently, this contribution is referred to as the osmotic or mixing interaction. The interaction energy (V_m) for the mixing interaction can be found from the Fisher theory (25). For a spherical particle with radius a is given by:

$$\frac{V_m}{kt} = \frac{4\Pi\varphi_2^2}{3v_1}\left(\tfrac{1}{2} - \chi\right)\left(\delta - \frac{H}{2}\right)\left(3a + 2\delta + \frac{H}{2}\right) \qquad [2.18]$$

Where φ_2 is the volume fraction of the surfactant in the adsorbed layer, v_1 is the volume of a solvent molecule, δ is the thickness of the adsorbed layer, and χ is the Flory-Huggins interaction parameter for the surfactant chain.

Equation [2.18] predicts that when $H < 2\delta$, V_m will start to increase since the adsorbed layers start to overlap. When $\chi < 0.5$, (ie. when the chains are in a good solvent) $V_m > 0$. Under the θ conditions for the chain ($\chi = 0.5$) $V_m = 0$. In a poor solvent where there are worse than θ conditions (ie. $\chi > 0.5$), $V_m < 0$ and the particles are attracted to one another.

The second contribution to steric interactions occurs when the chains in overlapping layers are compressed. This leads to a reduction in the configurational entropy of the chains since the volume available to them is reduced. This contribution is sometimes called the "volume restriction" effect. It contributes a term V_{vr} to the total energy of the steric interactions. A theory due to Mackor and Van der Waals (26) allows V_{vr} to be calculated according to equation [2.19].

$$V_{vr} = N_s kT\theta_\infty (1 - H/\delta) \qquad [2.19]$$

Where N_s is the number of chains adsorbed per unit area and θ_∞ is the fraction of the surface covered by an adsorbed layer with the surfaces at infinite separation. Clearly, the volume restriction contribution becomes effective when $H < \delta$.

The total steric interaction energy is then simply obtained as the sum of the individual contributions.

$$V_s = V_{vr} + V_m \qquad [2.20]$$

2.4.3 D.L.V.O. Theory

The well known theory of Derjaugin, Landau, Verwey and Overbeek (D.L.V.O.)

(27) assumes that the total interaction energy (V_t) between two particles containing adsorbed surfactant layers is given by equation [2.21].

$$V_t = V_e + V_a \qquad [2.21]$$

This theory allows for no steric contribution to the interparticle interaction energy.

Figure 2.3 shows the form of the energy - distance curve as predicted by the D.L.V.O. theory. V_{max}, $V_{min,1}$, and $V_{min,2}$ are the three major features of the plot of V_t vs. H. The magnitudes of these three parameters are determined by the factors affecting V_e and V_a (eg. Hamaker constant).

Tadros (25) has considered how the state of the suspension (slurry) is determined by the relative magnitudes of V_{max}, $V_{min,1}$ and $V_{min,2}$. If V_{max} is large (>>kt) and $V_{min,2}$ is shallow, then the particles are completely dispersed. Such conditions occur if the surface charge of a particle is high and the electrolyte concentration is low. This situation would arise if ionic surfactant molecules were adsorbed on the particle surface so that they were oriented perpendicularly to the particle surface.

If $V_{max} <$ 5-10 kT or is absent then the particles can coagulate, since

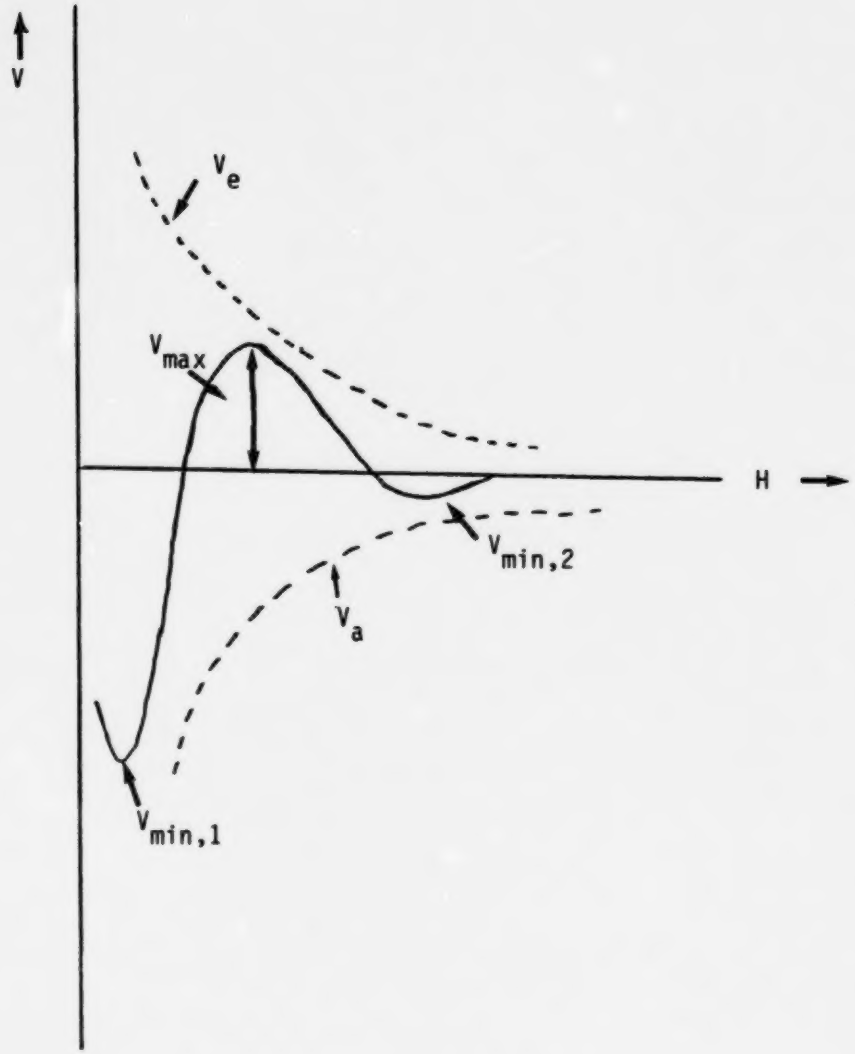


Figure 2.3 Interaction energy as a function of interparticle distance according to the D.L.V.O. theory.

they can overcome the energy barrier (V_{max}) and enter the deep primary minimum ($V_{min,1}$). This situation can arise if there is a high concentration of electrolytes or there are only a few surfactant molecules.

Finally, if $V_{max} > 10$ kT and $V_{min,2} > 1$-5 kT, the particles are kept in a state of weak flocculation. In this state particles are held together by a weak attraction at distances roughly corresponding to the location of $V_{min,2}$. Such a state may be characterized by a three dimensional network which may be destroyed by applying a shearing force. In situations where static stability is important, this may be the most desirable state. The addition of an intermediate concentration of electrolytes to a dispersed suspension can produce this state.

2.4.4 Steric Stabilization

The D.L.V.O. theory cannot account for the high stability that some non-ionic, macromolecular surfactants can produce in suspensions. This can be attributed to its failure to include the effect of steric interactions. Thus, a more complete version of equation [2.22] could be written as:

$$V_t = V_e + V_a + V_s \qquad [2.22]$$

In the case where a macromolecular or non-ionic surfactant is used, V_s

would be the dominant contribution for $H < 2\delta$. In the presence of a thick adsorbed layer (which might be expected with such surfactants) V_e becomes insignificant. V_t can therefore be considered to arise only from V_a and V_s. The form of the total interaction energy-distance curve is shown in figure 2.4.

The depth of the single minimum (V_{min}) depends on the thickness of the adsorbed layer and the Hamaker constant of the surfactant. If V_{min} is shallow, a well dispersed system is obtained. The rapid increase in V_t for $H < 2\delta$ prevents any strong aggregation of the particles. Consequently, extremely stable systems are possible with steric stabilization.

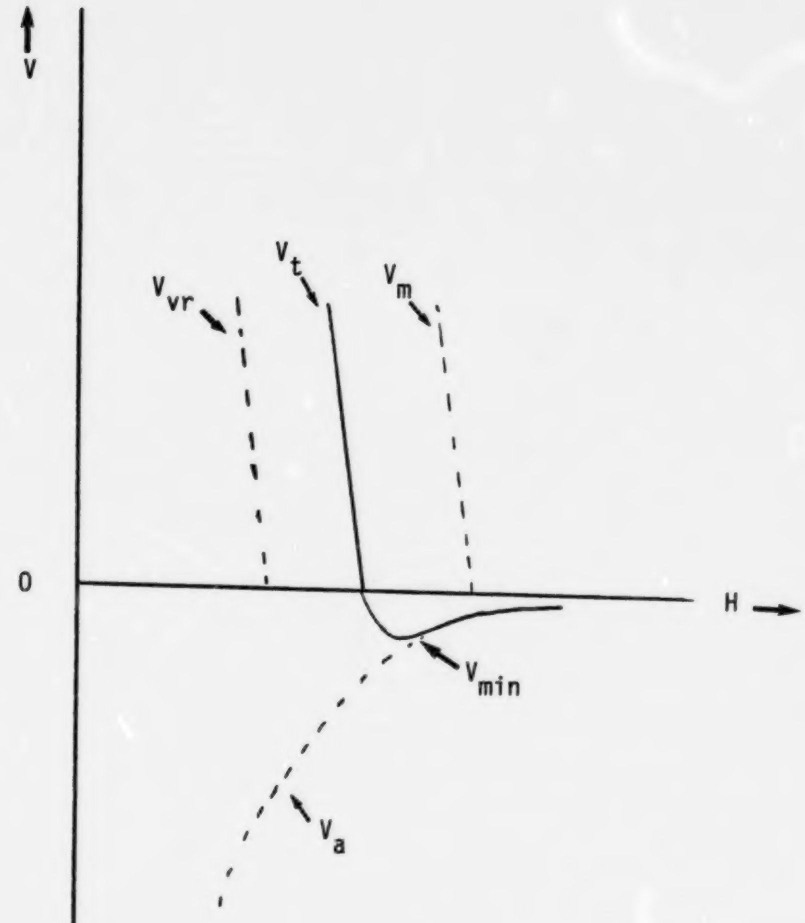


Figure 2.4 Interaction energy as a function of interparticle distance for a sterically stabilized system.

3.0 PRACTICAL ASPECTS OF SLURRY PREPARATION

3.1 Critical Solids Concentration

The behavior of finely divided solids that are dispersed in liquid media has been widely studied by those in the paint industry. Many useful concepts that have been applied to paint formulation have been virtually ignored in the development of slurry fuels. This is surprising in view of the obvious similarities between paints and slurry fuels. One concept that has found limited use in the production of coal slurries is the "critical solids volume concentration" or CSVC.

As a liquid is added to a fixed amount of a powdered solid, the liquid progressively displaces the air from the spaces between the solid particles. A three phase system (air, liquid and solid) exists until a point is reached where all of the air has just been displaced. At this point the space between the solid particles are filled with liquid, leaving only two phases in the system. The unique point at which this transition occurs is referred to as the CSVC of the system (28). If additional liquid is added to system at the CSVC, the interparticle distances become increasingly larger and interparticle forces become increasingly smaller.

The CSVC can also be reached by adding the solid to a fixed amount of liquid until the volume of liquid is just sufficient to fill the interstitial space within the powder bed. If more solid is added to a system at the CSVC. air pockets are formed within the system. Thus, the CSVC represents the maximum volume concentration of solid that can be dispersed in a liquid while maintaining only a liquid and a solid phase.

The CSVC is highly dependent on the packing density of the solid particles (28). Consequently, the particle sizes and their distribution can have a large effect on the CSVC. Generally speaking, increasing the number of small particles increases the CSVC by providing more efficient packing than is achievable with larger particles. On the other hand, particle agglomeration tends to reduce the CSVC since the larger agglomerates cannot be packed as densely as the individual particles can be.

Surfactants that inhibit agglomeration would therefore be expected to increase the CSVC. It has been reported that the maximum volume concentration of coal in a typical aqueous slurry is about 45% (53 wt%) in the absence of surfactants. The addition of a surfactant at levels as low as 0.5 wt% can increase this to about 63% (70 wt%) (29). This illustrates one of the major roles of surfactants in slurry formulation that is only rarely discussed in the slurry literature.

3.2 Settling Of Solid Particles In A Slurry

If a slurry is allowed to sit undisturbed for a prolonged period of time, gravitational forces cause the particles to gradually settle to the bottom of the container. In the absence of factors that interfere with settling, a very compact sediment that is very difficult to redisperse can form. Table 3.1 shows several factors that affect particle settling in slurries.

Clearly, the rate of settling can be controlled by reducing the particle size and/or increasing the viscosity of the liquid medium. Such treatment will only slow settling but it won't stop it. Patten (28) has suggested three classes of settling patterns for suspensions that can be distinguished on the basis of their appearance. These are shown in figure 3.1 . The least desirable of the three is obviously the "free" settling case since it results in a compact sediment that is very difficult to redisperse. In the other two cases the sediment is loose and easily redispersed.

Particle flocculation produces larger particles that settle more rapidly than their constituent particles would on their own. Smaller particles are entrained in this process and are dragged down with the flocculates resulting in a supernatant that is generally clear. Although the initial rate of settling is greater than that obtained with free settling, it stops at a point where the sediment is still loose and bulky. Sedimentation usually stops because a network that is strong enough to resist further settling is formed during flocculation. This structure is weak enough to be easily destroyed with mild agitation (ie. the structure is thixotropic). Thus, redispersal is easily achieved. However, vibrations such as those encountered in transportation can disrupt this

Table 3.1 Factors influencing particle settling.*

MAJOR FACTORS

1. PIGMENT PARTICLES

    size distribution
    shape
    density

2. SUSPENDING MEDIUM

    viscosity profile
    density

3. PARTICLE/MEDIUM INTERACTIONS

    degree of dispersion (flocculation vs. deflocculation)

4. ADDITIVES

    effect on interface activity and medium viscosity

5. SETTLING ENVIRONMENT

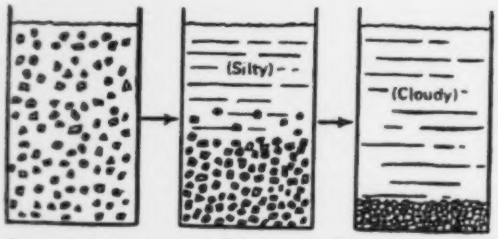
    undisturbed vs. disturbed (say during shipping)

IMPORTANT MINOR FACTORS

1. The density and viscosity of the medium can be modified by the presence of the suspended particles.
2. An upward medium velocity usually develops because of displaced medium (thus, apparent settling is less than actual settling).
3. Since smaller particles are entrained and dragged downward by large particles, they tend to exhibit an accelerated settling.
4. Flocculation is encouraged by the closely spaced particles in a concentrated suspension.

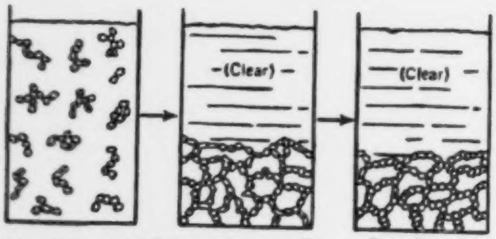
* reference (28).

Settling of dispersed (deflocculated) particles.



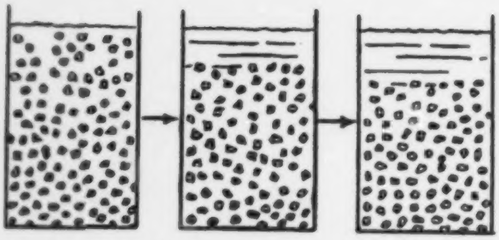
Persistent settling to hard-packed cake that resists redispersion.

Settling of flocculated particles.



Rapid settling to soft voluminous sediment that is easily redispersed.

Suspension of dispersed particles by colloidal structure.



Perfectly to nearly perfectly dispersed suspension provided by colloidal structure.

Figure 3.1 Schematic illustration of three types of idealized settling patterns.

network, permitting the sediment to settle into a compact cake.

Unfortunately the stability that is achieved by particle flocculation is obtained at the expense of some departure from the dispersed state. As the original purpose for grinding and dispersing the solid was to achieve a dispersed state, it follows that a large degree of flocculation is counterproductive. The most desirable method to achieve stability is to employ a material that provides a colloidal structure. Such stabilizers provide excellent static stability while preserving good particle dispersion.

Generally, these materials are used at very low concentrations (1%) but they can increase the viscosity of the liquid medium by as much as five orders of magnitude (30). Moreover this increase occurs only at low shear rates (such as those exerted by settling particles) and virtually disappears at high shear rates (such as those exerted during pumping).

3.3 Hydrocolloids Used As Stabilizers

3.3.1 Polysaccharides

The most widely used hydrocolloids are polysaccharides which are usually derived from natural sources. Table 3.2 shows a list of several common polysaccharides that are used as stabilizers along with their sources. The products derived from seeds, fruits, trees and seaweeds are referred

Table 3.2 Commonly used polysaccharides and their sources.*

POLYSACCHARIDE	SOURCE
alginates	brown seaweed
propylene glycol alginate	derivative of alginate
agar	red seaweed
carrageenan	red seaweed
locust bean gum	endosperm of tree seed
guar gum	endosperm of plant seed
tragacanth	exudate from bark of shrubs
gum arabic	exudate from tree bark
pectin	citrus peel and apple pomace
pectin amide	derivative of pectin
microcrystalline cellulose	hydrolyzed a-cellulose
methyl cellulose	cellulose derivative
hydroxypropyl cellulose	cellulose derivative
hydroxypropyl methyl cellulose	cellulose derivative
ethyl methyl cellulose	cellulose derivative
carboxymethyl cellulose	cellulose derivative
starch	cereal and roots
starch derivatives	cereal and roots
xanthan gum	bacteria

* reference (30).

to as gums. Table 3.3 shows the relative distribution of polysaccharides as a function of their general properties. It is clear from this data that these materials are used primarily as thickening and suspending agents.

The diversity of the industrial uses of these polysaccharides is illustrated by the data shown in table 3.4. Clearly, there is no single industrial application for these materials. On the basis of their utility as thickeners and their widespread industrial use, it is not surprising that these materials have also been widely used in the preparation of aqueous coal slurries (31-42).

The data in table 3.5 show a breakdown of the U.S. consumption of industrial polysaccharides in 1979. The gums listed in table 3.5 can be considered to be natural gums with the exception of methyl cellulose and carboxymethyl cellulose. xanthan gum is unique among the natural gums listed in this table in that it is derived from a microbial source. Natural gums (with the exception of xanthan gum) are subject to fluctuations in quality and quantity as their production can be seriously affected by adverse weather conditions. This makes their cost and availability unpredictable. On the other hand, microbial gums can be produced under carefully controlled conditions. Consequently, they can be supplied with more consistency of purity, supply and price than other gums. The rheology and chemistry of the various polysaccharides have been reviewed in detail in references (30) and (43). The reader is directed to

Table 3.3 Distribution of polysaccharides according to functional properties.*

FUNCTION	PERCENTAGE
stabilizer, suspending agent and dispersant	25
thickener	23
film-forming agent	17
water-retention agent	12
coagulant	7
colloid	6
lubricant or friction reducer	5
other	5

* reference (30).

Table 3.4 Distribution of polysaccharides according to industrial usage.*

INDUSTRIAL USE	PERCENTAGE
detergents and laundry products	16
textiles	14
adhesives	12
paper	10
paint	9
food	8
pharmaceutical and cosmetic	7
other	24

* reference (30).

Table 3.5 Consumption of polysaccharides in the United States.*

POLYSACCHARIDE	CONSUMPTION FOOD Mlb	INDUSTRIAL Mlb	TOTAL Mlb
corn starch	600	2500	3100
corn sugars	12000	-	12000
agar	0.3	0.4	0.7
gum arabic	24.0	7.0	31.0
alginates	10.0	2.0	12.0
carrageenan	9.0	0.2	9.2
gum ghatti	10.0	1.0	11.0
guar gum	20.0	45.0	65.0
karaya gum	1.0	7.0	8.0
locust bean gum	9.0	3.0	12.0
pectin	12.0	-	12.0
methyl cellulose	2.0	53.0	55.0
carboxymethyl - cellulose	16.0	100.0	116.0
tragacanth	1.3	0.2	1.5
xanthan gum	3.0	9.0	12.0

* reference (30).

these references for additional information on these materials.

3.3.2 Clay Minerals

Several types of clay minerals have been used as stabilizers in coal-water slurries. The most frequently used of these clays have been colloidal grades of: attapulgite, sepiolite and Wyoming bentonite (44,45). Such clays form thick gels in water at concentrations of about 10 wt%. At lower concentrations (<1 wt%) the colloidal clay particles flocculate to form a loose supporting network similar to that previously described above. As the stabilizing influence of these materials depends on flocculation of the colloidal clay particles, care must be taken to ensure that any surfactant used in the system does not inhibit flocculation of the clay. If this process is inhibited, there will be little or no stability provided by the clay.

4.0 SURFACTANTS CURRENTLY USED IN SLURRY PREPARATION

4.1 Commercial Surfactants

Over the past few years there has been a tremendous growth in the volume of work that deals with slurry fuels and feedstocks. The primary focus of most of this work has been coal-liquid slurries. The liquids have generally been: oil (46-58), water (31-42,59-119) or alcohol (120,121). Some of this work has also dealt with other carbonaceous materials such as petroleum coke (59,60) and pitch (122-127).

In order to achieve high efficiencies in transportation or final processing, these slurries should have high solids content. Additives such as surfactants have been used to achieve high solids content while reducing negative side effects of high solids content in slurries of all types. The present discussion will be limited to a consideration of such surfactant additives in only aqueous slurries.

An extensive research program has been carried out in Japan by Kao Soap Co. Ltd. and Lion Corp. in cooperation with several leading Japanese heavy industrial concerns (112). This study has involved the evaluation of two thousand additives for aqueous slurries of twelve different types of coal. Well over one hundred of these and other materials have appeared in the Japanese patent literature. The coal (or coke) which is used in these patents is usually ground so that 80% of it passes a 200 mesh screen. The slurries usually contain between 70 and 75% solids by weight and 0.25 to 2% additive based on the slurry weight. These slurries are reported to be stable for months and their viscosities are reduced by about 50 to 75% as a result of the presence of the additive. Similar efforts on a somewhat smaller scale have also been undertaken throughout Europe.

The additives are generally either anionic or nonionic surfactants since these materials are generally the least expensive surfactants. Nonionic surfactants which have been patented are frequently copolymers (99,113) or the derivatives of copolymers of ethylene oxide and propylene oxide. For example ethylene oxide and propylene oxide have been added to: sorbitol (114), glycerol (80), fatty alcohols such as lauryl alcohol (81,90), lauric acid (115) or styrene oxide and glycerol (116) to yield high molecular weight esters. Fatty acid alkylenediamine or alkylenetetramine condensates have been prepared by adding ethylene oxide and propylene oxide to triethylenetetramine and stearic acid (59,83,111).

Several anionic surfactants have also appeared in the Japanese patent literature. Many of these materials are formaldehyde condensates of: naphthalene sulfonic acid (60,91), lignosulfonic acid and naphthalene sulfonic acid (117), or naphthalene sulfonic acid and phenol sulfonic acid (118). The salts of various copolymers of ethylene oxide, acrylic acid and maleic acid (63,92) or acrylamide (62) have also been reported to be effective.

American patents have generally involved the use of commercially available surfactants or combinations of these surfactants with other additives (eg. stabilizers). Other work has been concerned with the effect of particle size distribution on the slurry properties. For example Funk (71-74,119) has described a slurry with a high solid content (70% by volume) in which the void space is minimized and the particle surface area is maximized. This is achieved by grinding the solid so that a particular particle size fraction is produced. He claims that this enhances the dispersing effects of the additives and increase the stability of the slurry so produced.

Mark (75-77) has reported that nonionic surfactants such as: nonylphenoxy poly(oxyethylenyl) ethanol (eg. Domtar IGEPAL series), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers (eg. B.A.S.F. PLURONIC F series) and condensation products of ethylene oxide, propylene oxide and ethylenediamine (eg. B.A.S.F. TETRONIC series) were effective only if they contained more than 100 ethylene oxide units.

Several anionic surfactants have also been patented in America for use in slurries of carbonaceous materials. Many patents have reported a substantial drop in the viscosity of such slurries when a surfactant is added. For example, the viscosity of an aqueous slurry of coal containing 60% by weight solids (80% of which could pass through a 200 mesh sieve) was reduced by 75% using salts of alkyl sulfosuccinates such bis-2-ethylhexyl sulfosuccinate (70). Similar results have been obtained using salts of the formaldehyde condensates of: dodecylbenzene sulfonic acid (65), arylphenol-sulfonic acid (64) and naphthalenesulfonic acid (69).

4.2 Surfactants From Low Cost Materials

Many of the current surfactants were originally obtained in a crude form as waste or byproducts of other processes. Surfactants such as: lignosulfonates, fatty acid soaps, sulfomethylated hydroxy aromatics and alkylaromatic sulfonates were all originally obtained in some form from a byproduct stream. As the use of these materials widened, they were purified and modified chemically to improve their effectiveness. Some materials such as alkylaromatic sulfonates became valuable products in their own right. These materials were sometimes more valuable than the original primary product of the process from which they were produced (4).

Several commercial surfactants can still be obtained in a crude form from byproduct streams which are otherwise considered as waste. For example dilute solutions of lignosulfonates can be obtained from sulfite black liquor (a byproduct of the Kraft pulping process). Similarly, fatty acids can be obtained from meat processing wastes, rancid vegetable oil or tall oil. Petroleum acid pitch can serve as a source of alkylbenzene sulfonates. These materials may be much less expensive but they may also be much less effective than purified commercial surfactants.

Many waste streams may contain materials which can be reacted to produce highly effective surfactants. For example alkylenediamines could be reacted with ethylene oxide and propylene oxide to form a long chain nonionic surfactant. The effectiveness of crude tall oil can be improved by partial esterification with poly(ethylene) glycol (128). Poly (ethylene) glycol can itself be found in waste streams (129).

Some surfactants can be obtained from low cost "natural sources". For example, humic acids are complex, aromatic carboxylic acids that are formed from decaying vegetation. Thus, materials such as peat and low rank coals are excellent sources of humic acids. Recently, several patents have covered the extraction and sulfonation of humic acids from low rank coals and the subsequent use of the sulfonated humic acids as a surfactant in the preparation of aqueous coal slurries (86,109,130). The humic acid sulfonates are reported to be as effective as most lignosulfonates. Waxes obtained from peat and low rank coals have also been modified by reacting them with ethylene oxide. The resulting material is claimed to be an effective surfactant (131).

5.0 RHEOLOGY

5.1 Background

5.1.1 Introduction

Rheology is defined as the science of the deformation and flow of matter (132). It is primarily concerned with the deformation of cohesive bodies when they are subjected to some type of force. Deformation of a body can be divided, on a subjective basis, into two general types. Spontaneously reversible deformation is called elasticity while irreversible deformation is called flow. For the purposes of this work only flow will be considered.

The degree of deformation that is produced by a force acting on, or within, a body is dependent on the magnitude of the force per unit area and not on the magnitude. In rheology, the force per unit area is usually referred to as a stress. The force can be applied perpendicularly to the area (a tensile stress), tangentially to the area (a shear stress) or at any other angle to the surface of the body being deformed.

Figure 5.1 shows a deformation that is produced by a shear stress acting on a body. The shear stress (τ) is the shear force (F) per unit area (A) to which the force is applied and is defined in equation [5.1].

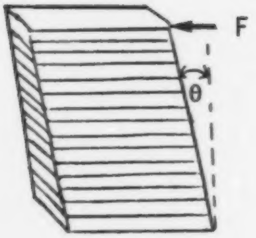


Figure 5.1 A simple deformation caused by a shear stress.

$$\tau = \frac{F}{A} \qquad [5.1]$$

Although the nature of the deformations induced by such stresses can be limitless, the most important deformation for the purposes of this work is called shear. Simple shear is a process in which infinitely thin, parallel planes slide over each other, as in a pack of cards. This type of deformation is associated with a shear stress. As shown in figure 5.1, the shear stress causes an angular displacement of a plane within the body that is parallel to the shear stress itself, relative to other parallel planes within the body. The shear strain (γ) is a measure of the magnitude of the shear. This quantity is simply the ratio of the displacement between any two planes to the distance between them. Equation [5.2] defines the shear strain in terms of the angular displacement θ shown in figure 5.1.

$$\gamma = \mathrm{TAN}(\theta) \qquad [5.2]$$

The rate of change of the shear strain with respect to time ($\dot{\gamma}$) is known as the shear rate. Viscosity (η) is simply defined in equation [5.3] as the ratio of shear stress to shear rate under laminar flow conditions (133).

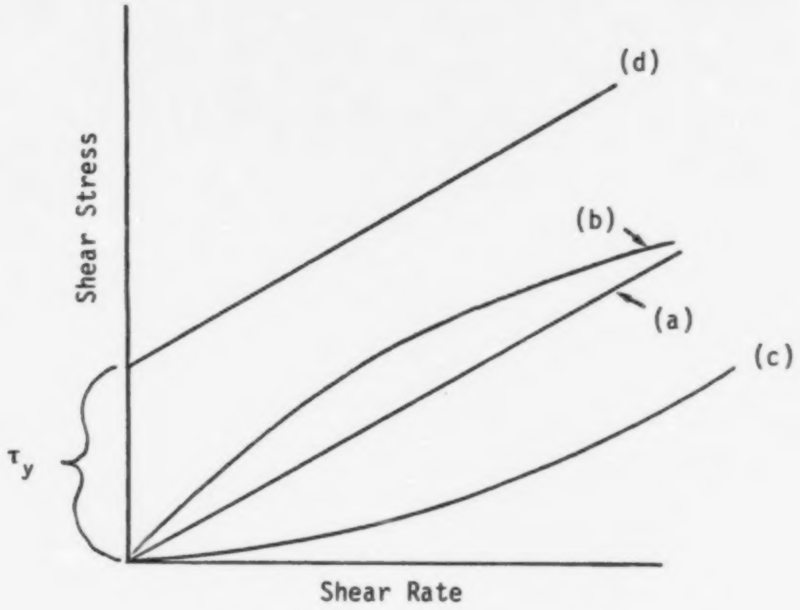
$$\eta = \frac{\tau}{\dot{\gamma}} \qquad [5.3]$$

It can be considered to be the "frictional" resistance to the motion of the parallel planes within a fluid past one another, under the influence of a shear stress (132,133).

The materials which exhibit the simplest rheological behavior are known as Newtonian fluids. Newtonian fluids display a simple linear relationship between shear stress and shear rate (see figure 5.2). Thus, the viscosity of a Newtonian fluid is independent of shear rate. Figure 5.3 shows the shear rate dependence of the viscosity of a typical Newtonian fluid. Such simple behavior permits rheological measurements of Newtonian fluids to be accomplished with very simple and inexpensive instruments. Unfortunately Newtonian behavior is generally limited to low molecular weight, single phase liquids. Most other fluids exhibit some type of non-Newtonian behavior.

Non-Newtonian behavior is characterized by a non-linear relationship between shear stress and shear rate. Consequently, the viscosity of a non-Newtonian fluid will depend on the shear rate. This type of behavior is probably attributable to mechanical factors peculiar to the particular fluid. Such factors may include for example, the destruction of the loose aggregates that are present in flocculated dispersions when a shear stress is applied. The extent of the destruction of these aggregates may be dependent on shear rate and the duration of the applied shear stress. This would certainly affect the size and shape of the aggregates which in turn would affect the force required to move them. Thus, considerable changes in the observed viscosity of the dispersion could be effected by

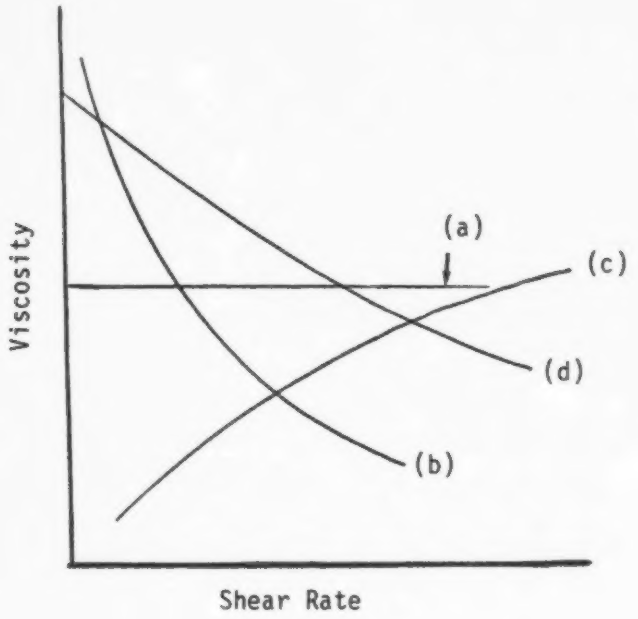
Figure 5.2 Shear stress as function of shear rate for various ideal rheological bodies.



Key:

(a) Newtonian flow, (b) Pseudoplastic flow, (c) Dilatant flow, (b) Plastic flow.

Figure 5.3 Viscosity as a function of shear rate for various ideal rheological bodies.



Key:

(a) Newtonian flow, (b) Pseudoplastic flow, (c) Dilatant flow, (d) Plastic flow.

changing the shear rate and/or the duration of the applied shear stress.

Different types of Non-Newtonian behavior are frequently separated into several general categories. However, the distinctions between these categories can become blurred at times since different classes of behavior may be observed at different shear rates. The most commonly encountered categories of non-Newtonian behavior are: pseudoplasticity (shear thinning), dilatancy (shear thickening), plasticity, thixotropy and rheopexy. Figures 5.2 and 5.3 show behavior that is typical of each of these categories.

The first three of the above listed categories describe behavior that is only a function of shear rate. Pseudoplastic materials display decreasing viscosities with increasing shear rate. This type of behavior is exhibited by a wide variety of fluids including paints, emulsions and other dispersions. On the other hand, the viscosity of dilatant materials increases with increasing shear rate. Although this type of behavior is less frequently encountered than pseudoplasticity, it is often observed in dispersions that contain high concentrations of deflocculated particles such as corn starch in water or sand/water mixtures. Plastic fluids behave as solids under static conditions. These fluids will only flow when the applied shear stress exceeds a certain value. The shear stress that is required to induce flow is called the yield value. Once flow begins, a plastic material can exhibit pseudoplastic or dilatant flow characteristics. The most familiar example of a plastic material may be tomato ketchup. Frequently, ketchup will not pour from the bottle until the bottle is tapped or shaken because of its yield value. The action of tapping or shaking the bottle provides the shear stress that exceeds the yield value and permits flow to occur.

The final two categories are associated with time dependent viscosity changes under constant shear conditions. Fluids that exhibit decreasing viscosities with time while subjected to constant shearing are called thixotropic. Rheopectic fluids display an increasing viscosities with time while they are subjected to constant shearing. While thixotropy is quite common (thixotropic fluids include materials such as paints and greases); rheopexy is extremely rare. Both rheopexy and thixotropy can be found in combination with any of the aforementioned categories of rheological behavior. The nature of the time dependence that is the characteristic of these two classes of rheological behavior is highly dependent on the: shear conditions, nature of the fluid and the history of the fluid. This can complicate rheological measurements since the results obtained with such fluids will depend on how long the sample has been left undisturbed before the measurements are made and its prior shear history.

5.2 The Yield - Power Law

Several largely empirical equations have been developed to describe the wide variety of flow behaviors that are encountered in rheological studies (133). One of the most flexible and widely used of these is the yield-power law given by equation [5.4].

$$\eta = \frac{\tau_y}{\gamma} + \alpha(\dot{\gamma})^{n-1} \qquad [5.4]$$

Where τ_y is the yield value and α and n are constants known respectively as the coefficient of rigidity and the flow index.

The substitution of appropriate values of τ_y, α and n into equation [5.4] can yield a reasonably good description of many of the rheological behaviors previously described. For example if $\tau_y = 0$ and $n = 1$, equation [5.4] becomes a description of a Newtonian fluid. If $\tau_y = 0$ and n 0 or n 0 then a reasonable description of pseudoplastic or dilatant behavior is obtained respectively (although not at extremely low or extremely high shear rates). Finally, if τ_y is non-zero and $n = 1$ then the fluid is called a Bingham plastic. There have been many efforts to adapt equation [5.4] to include the time dependent effects of thixotropy and rheopexy but these have not found general acceptance (132,133).

5.2 Slurry Rheology

The potential utility of any slurried fuel will be determined by its static stability, pumpability and its performance as a fuel (134). These important properties are themselves determined by the rheological properties of the slurry. It is believed that low shear rate ($< 10\ S^{-1}$) rheology determines the static stability of a slurry since particle sedimentation occurs under the low shear rate conditions imposed by gravity (119,135,136). The pumpability of a slurry is governed by its viscosity at shear rates that are characteristic of pumping (10-200 S^{-1}) (134,135,137). Finally, the performance of the slurry as a fuel is frequently governed by its atomization properties since smaller droplets may improve the efficiency of combustion or gasification. The atomization properties of a given slurry are determined in turn by its viscosity at the high shear rates (2000-30,000 S^{-1}) that are required for atomization (134,136-138).

The rheology of aqueous, slurried fuels is known to be extremely complex (134-145). In many cases these fluids can possess yield values (134,136,139,140) and a given slurry may exhibit pseudoplastic, dilatant and even Newtonian behavior over certain ranges of shear rates (134,135,136,141). Moreover, the rheology of these slurries is known frequently to depend on shear history. Thus, both thixotropy (136,142) and rheopexy (136) are also frequently observed. Generally, a suitable slurried fuel should possess a sufficiently large yield value to inhibit particle settling under static conditions. It is also desirable that the viscosity of the slurry be as low as possible at shear rates associated with pumping and atomization. Thus, plastic behavior with pseudoplastic flow is the most desirable rheological behavior for a good slurried fuel (134,136,141). Such behavior is described by equation [5.4] with $n < 1$.

The bulk of the rheological studies of slurried fuels carried out in the past have focussed on the improvement of the rheological properties for a particular phase of utilization, through chemical additives such as surfactants and stabilizers (135,139,142-145). Other work has focussed on the rheological effects of such parameters as particle size distribution of the dispersed solid (134,137,140,145) and solids concentration (134,135,137,140). Unfortunately, there has been no standardized procedure either for measuring the rheological properties of the slurries or for analyzing the data. This makes interpreting the literature difficult, particularly if there is evidence of thixotropy. However, the following generalizations may be made: non-Newtonian behavior becomes more pronounced as the solids concentration increases, narrow particle size distributions lead to higher viscosities at all shear rates (particularly for very fine particle size distributions), the viscosity increases dramatically as the solids concentration approaches the critical solids volume concentration (see section 3) and finally, the addition of small amounts of surfactants can greatly change the rheological properties of a given slurry.

6.0 MATERIALS AND METHODS

6.1 Materials

6.1.1 Pitch

6.1.1.1 CANMET Hydrocracked Pitch

Approximately 7.5 kg of CANMET hydrocracked pitch were received from CANMET in Ottawa. A sample of this material was submitted to the CANMET Energy Research Laboratories, Fuels Characterization Research Laboratory for analysis. The results of this analysis are given in Table 6.1.

6.1.1.2 PETRO-CANADA Hydrocracked Pitch

Approximately 20 kg of PETRO-CANADA were obtained from CANMET in Ottawa. A sample of this material was analyzed at the CANMET Energy Research Laboratories, Fuels Characterization Research Laboratory. The results of this analysis are shown in table 6.2.

6.1.2 Additives

Several commercial surfactants were selected after: surveying the current patent literature concerning slurry fuel preparation, consulting with the surfactant manufacturers and preparing a small number of test slurries. On this basis, the following surfactants were selected:

Table 6.1 Analysis results for a sample of CANMET hydrocracked pitch.

ANALYSIS PERFORMED	RESULT wt%
(proximate, as analyzed)	
MOISTURE	0.01
ASH	5.24
(ultimate, as analyzed)	
C	79.96
H	6.11
N	1.35
S	5.40
O (by diff.)	1.93
(minerals in ash by I.C.P.)	
SiO_2	44.18
Al_2O_3	25.95
Fe_2O_3	11.94
TiO_2	3.17
P_2O_5	0.00
CaO	3.13
MgO	1.37
SO_3	0.00
Na_2O	0.50
K_2O	1.66
BaO	0.11
SrO	0.05
MnO_2	1.09
V_2O_5	3.31
NiO	0.00

Table 6.1 Analysis results for a sample of CANMET hydrocracked pitch. (Continued.)

ANALYSIS PERFORMED	RESULT wt%
(minerals in ash, by I.C.P.)	
Co_3O_4	0.16
MoO_3	0.00
SnO_2	0.16
ZnO	0.04
CuO	0.00
LOF	0.69

Table 6.2 Analysis results for a sample of PETRO-CANADA hydrocracked pitch.

ANALYSIS PERFORMED	RESULT wt%
(proximate, as analyzed)	
ASH	1.43
(ultimate, dry)	
C	86.44
H	7.05
N	1.32
S	2.87
O (by diff.)	0.89

(1) PLURONIC F-108 (B.A.S.F. CANADA, INC., MONTREAL, P.Q.)

- A nonionic poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) block copolymer.
- Molecular weight 14,000.
- 255 ethylene oxide units.

(2) TETRONIC 1508 (B.A.S.F. CANADA,, INC., MONTREAL, P.Q.)

- A nonionic poly(oxyethylene)-poly(oxypropylene) block copolymer -ethylene diamine condensate.
- Molecular weight 17,000.
- 309 ethylene oxide units.

(3) ANTAROX DM-970 (GAF (CANADA) INC., MISSISSAUGA, ONT.)

- A nonionic nonylphenoxy(poly(oxyethylenyl))ethanol.
- Molecular weight 66946.
- 150 ethylene oxide units.

(4) ANTAROX DM-730 (GAF (CANADA) INC., MISSISSAUGA, ONT.)

- A nonionic nonylphenoxy(poly(oxyethylenyl))ethanol.

(5) MASIL 2133 (MAZER CHEMICALS CANADA (INC.), MISSISSAUGA, ONT.)

- A nonionic silicone glycol copolymer.

(6) LOMAR D (DIAMOND SHAMROCK CANADA LTD., HAMILTON, ONT.)

- Anionic.

- The sodium salt of a condensed naphthalene sulphonic acid.

(7) FENOPON TK-32 (GAF (CANADA) INC., MISSISSAUGA, ONT.)

- Anionic.
- Sodium N-methyl-N-Tall oil acid Taurate.

(8) LIGNOSOL XD (REED LIGNIN, QUEBEC, P.Q.)

- Sodium lignosulphonate.

(9) LIGNOSOL TSD (REED LIGNIN, QUEBEC, P.Q.)

- Ammonium lignosulphonate.

(10) LIGNOSOL BD (REED LIGNIN, QUEBEC, P.Q.)

- Calcium lignosulphonate.

(11) MARASPERSE CBX-2 (REED LIGNIN, QUEBEC, P.Q.)

- Sodium lignosulphonate.

(12) MARASPERSE CBOS-3 (REED LIGNIN, QUEBEC, P.Q.)

- Sodium lignosulphonate.

All of the above with the exception of MASIL 2133 and ANTAROX DM-730 were used in the preparation of slurries containing CANMET hydrocracked pitch. Slurries containing PETRO-CANADA hydrocracked pitch were prepared with each of the above listed surfactants with the exception of FENOPON TK-32.

6.2 Methods

6.2.1 Grinding

6.2.1.1 CANMET Hydrocracked Pitch

The CANMET hydrocracked pitch provided by CANMET was in various states of comminution. Consequently, different degrees of grinding were required with each sample of pitch in order to obtain the desired particle size distribution (PSD). In general, the pitch was first pulverized in a cast iron mortar and pestle. The pulverized pitch was then fed into a Retsch cross beater grinding mill (at CANMET in Ottawa). It was necessary to grind the pitch three times using increasingly fine mill screens each time.

Two PSD's were prepared for this work. In the first PSD, 100 % of the particles were -325 mesh. The distribution obtained for the the second PSD is shown in Table 6.3. For the purposes of this work, the first PSD will be referred to as the -325 mesh pitch while the second PSD will be referred to as the -200 mesh pitch. In order to prepare the -325 mesh pitch, the following sequence of mill screens were employed on the three grinds: (1) 1.00, (2) 0.25 and (3) 0.08. The preparation of the -200 mesh pitch required the following sequence of mill screens: (1) 1.00, (2) 0.50 and (3) 0.25, on the three grinds.

Table 6.3 Particle size distribution of -200 mesh CANMET hydrocracked pitch.

SIZE CONSIST*	FRACTION OF TOTAL MASS wt%
+100	0.0
100x200	20.0
200x325	62.5
-325	17.5

* Where 100x200 means the sample passed a 100 mesh screen but not a 200 mesh screen.

Throughout the grinding procedure, it was necessary to periodically disassemble the mill and inspect it for signs of clogging. Clogging occurred when pitch particles would melt and adhere to the mill screen during the grinding process. The molten pitch would then trap more pitch particles which would also melt. This process would continue until the mill would no longer operate. This was especially true when using the number 0.08 mill screen.

6.2.1.2 PETRO-CANADA Hydrocracked Pitch

The PETRO-CANADA hydrocracked pitch was obtained from CANMET in the form of large chunks which had to be pulverized with a mortar and pestle prior to grinding. This pitch was much softer than the CANMET hydrocracked pitch. Attempts to treat the pulverized pitch in the same fashion as that the CANMET hydrocracked pitch were singularly unsuccessful.

In the first place, the mill became clogged with molten pitch almost as soon as the grinding process was initiated with the number 1.00 mill screen. Consequently, it was necessary to employ a cryogenic grinding technique in an effort to minimize the production of molten pitch. The application of this technique involved the following procedure.

A mixture of approximately equal amounts of pulverized pitch and pulverized dry ice was prepared. This mixture was then ground using the Retsch cross beater mill and the number 1.00 mill screen. The pitch ground in this way was then mixed with an equal amount of pulverized dry ice and ground again using finer mill screens. Occasionally it was necessary to employ liquid nitrogen to cool the pitch when dry ice was unavailable. This procedure reduced the magnitude of the "mill clogging" problem to a level that was comparable to that encountered when grinding the CANMET hydrocracked pitch using the number 0.08 mill screen. However, even with cooling it was not possible to grind the PETRO-CANADA hydrocracked pitch using the number 0.08 mill screen.

Secondly, problems were also encountered on attempting to perform a standard sieve analysis on the cryogenically ground pitch. Once this material was allowed to reach room temperature, it became somewhat sticky and had a strong tendency to form aggregates. Consequently, when small quantities were placed on standard sieves and shaken, some of the material quickly became stuck to the screen. As the shaking continued, more and more pitch would adhere to the pitch that had stuck to the screen. Thus, the sieve screen rapidly became clogged with pitch.

Moreover, pitch particles also formed fairly large aggregates (about 1 mm in diameter) that would not pass through the screen even before it became clogged. Attempts to sieve the pitch while it was cold did not reduce either problem to an acceptable level. Therefore it was neither possible to perform a standard sieve analysis on this material nor was it possible to employ standard sieves to prepare different PSD's. However, it was possible to obtain particle size analyses using a Coulter counter at

CANMET.

Coulter counter analyses were performed on pitch samples that had been subjected to three different degrees of comminution in order to determine whether PSD's, that were similar to those obtained for the CANMET hydrocracked pitch, could be produced by varying the extent of the grinding process. The following following sequences of mill screens were employed for this purpose:

(1) number 1.00 only (singly ground),
(2) number 1.00, number 0.50 (doubly ground),
(3) number 1.00, number 0.50, number 0.25 (triply ground).

The results of these analyses are given in Table 6.4. It was decided that the singly ground pitch did not contain enough -200 mesh material to be useful. Moreover, it was evident that there was insufficient difference between the PSD's of the doubly and triply ground pitch to clearly establish the effect of varying PSD on the slurry characteristics. Consequently, only one PSD, prepared by cryogenically grinding the pitch using sequence (3), was employed in this work.

6.2.2 B.E.T. Surface Area Determination

The surface area of pitch samples were determined by nitrogen adsorption using a Micromeritics model 2200 high speed surface area analyzer. The surface area of a sample of -60 mesh Syncrude coke determined with

Table 6.4 Particle size distribution for PETRO-CANADA hydrocracked pitch, ground to different extents, as determined by Coulter counter analysis.

EXTENT OF GRINDING*	FRACTION OF PARTICLES IN SIZE CONSIST		
	+200 MESH vol%	200x325 MESH vol%	-325 MESH vol%
singly+	85	13	1
doubly	8	29	63
triply	6	17	77

* where: doubly ground pitch was ground using the number 1.00 mill screen and reground with the number 0.50 mill screen and triply ground pitch is doubly ground pitch that was reground with the number 0.25 mill screen.

+ It was necessary to screen out some of the largest particles for the Coulter counter analysis. Thus, material ground using only the number 1.00 mill screen was sieved using standard sieves. This value represents the PSD (as determined by the Coulter counter) for the 100x200 mesh size fraction. This size fraction constituted 81 wt% of the total material. Of the remaining material, 14 wt% was +100 mesh, 4.0 wt% was 200x325 and only 1.0 wt% was -325 mesh. Although sieving was not an effective means for separation of large quantities of pitch or for separating pitch particles that were smaller than 100 mesh, it was a fairly effective means for removal of the +100 mesh particles which were too large for the Coulter counter. It is likely that the 100x200 mesh material is most representative of the singly ground pitch.

this instrument was 7.2 m^2g^{-1}. This is in excellent agreement with the value (7.6 m^2g^{-1}) reported in reference (147) for a sample of the same material. Samples (2.5 to 3 g) of -325 mesh, 200x325 and 100x200 mesh CANMET hydrocracked pitch were initially degassed at 50 °C for 45 min. In all cases the surface area was below the detection limit of 0.01 m^2 total surface area. Increasing the degassing temperature to 80 °C yielded the same results. However, significant pitch fusion was observed at temperatures above 70 °C. In view of the problems encountered with grinding the PETRO-CANADA hydrocracked pitch, it was likely that fusion would occur at even lower temperatures. This would have necessitated even lower temperatures for degassing the sample - thereby casting doubt upon the validity of any result obtained.

6.2.3 Slurry Preparation

6.2.3.1 Ultrasonically Dispersed Slurries

Ninety six slurries were prepared in order to evaluate intense ultrasound as a means for mixing. Approximately 65 of these slurries contained 60 wt% pitch and various concentrations of: LIGNOSOL XD, LIGNOSOL TSD, LIGNOSOL BD, MARASPERSE CBX-2, MARASPERSE CBOS-3, LOMAR D, MASIL 2133, PLURONIC F-108, ANTAROX DM-730, ANTAROX DM-970 and TETRONIC 1508. The remaining slurries contained 50 wt% pitch and varying concentrations of the following surfactants: LIGNOSOL XD, LIGNOSOL TSD, LIGNOSOL BD, LOMAR D, and PLURONIC F-108. Surfactant concentrations of between 0.10 and 1.2 wt% were employed.

Slurries were prepared in 100 g batches, in a 150 ml pyrex beaker, using intense ultrasound with a frequency of 20 kHz and an acoustic intensity of 27 W cm^{-2}. The ultrasound was generated by a Bransonic W-350 Sonifier ultrasonic generator and was delivered to the slurry by a standard titanium coupling horn which was immersed directly in the slurry. A preweighed amount of PETRO-CANADA hydrocracked pitch was added to the appropriate mixture of additive and distilled water, in three batches each of which comprised roughly one third of the total material. Ultrasound was applied for about 5 min after each addition. The irradiation continued until the slurry appeared to be fluid or until the total irradiation time was 60 min. It was always necessary to augment the agitation provided by the ultrasound with substantial mechanical mixing with a stirring rod. If such mixing was not provided, the pitch would float on the surface of the liquid without becoming incorporated in it. The slurry was surrounded by a cold water bath in order to keep its temperature relatively constant during the irradiation.

6.2.3.2 Mechanically Dispersed Slurries

Slurries were prepared in 100 g batches using a Hamilton Beach "Drinkmaster" high speed disperser for mixing. The ingredients were weighed directly into the stainless steel mixing vessel (about 250 ml in volume). The slurry was then mixed at low speed for 5.0 min, followed by 25 min of high speed mixing. Shorter mixing periods generally resulted in poor pitch incorporation. Complete incorporation of the pitch into the slurry was not always achieved even after mixing for 30 min. In these cases, mixing periods of up to 60 min were no more effective. A qualitative assessment of the slurry consistency was then made.

When slurries containing either type of pitch were prepared there was a slight increase in temperature during the mixing phase. This temperature increase was sufficient to cause some fusion of the PETRO-CANADA hydrocracked pitch which lead to the formation of large granules of solid pitch. Consequently, cooling was provided during mixing of the PETRO-CANADA hydrocracked pitch slurries by surrounding the mixing vessel with a cold water bath.

6.2.4 Storage

After the slurries were prepared, they were immediately transferred to 100 ml graduated cylinders, sealed with 5 layers of Parafilm and allowed to sit undisturbed on the bench top for 1 week. In some cases a significant amount of material adhered to the wall of the cylinder. In these cases the adhering material was scraped into the bulk slurry using a spatula before the tubes were finally sealed. No attempt was made to thermostat the samples other than that provided by the room thermostat. Slurries in which the pitch was not completely incorporated were discarded after mixing and were not stored.

6.2.5 Penetration Test

6.2.5.1 Apparatus

The consistency of the sediment in each slurry was evaluated after one week using a penetration test. The apparatus that was used was similar to one described in reference (148) and is shown in figure 6.1. It consisted of a 3 mm aluminum rod with a polyethylene disc (1.5 cm in diameter) glued to one end. One end of this rod could be placed through the centre of a guide ring. This guide ring could then be placed on top of a given test cylinder such that the plastic disc would penetrate the slurry. A light weight plastic cup could then be placed on the end of the rod (opposite to that attached to the disc). The depth to which the rod penetrated was determined visually using a scale. Known weights could be placed in the cup and the change in penetration depth determined.

6.2.5.2 Procedure

The penetration rod was placed through the guide ring which was then placed on top of the cylinder containing the slurry to be tested. The scale was then positioned and the rod released manually. A timer was started as soon the rod was released. If the penetration depth of the rod had not changed after 1 min, the penetration depth of the rod was

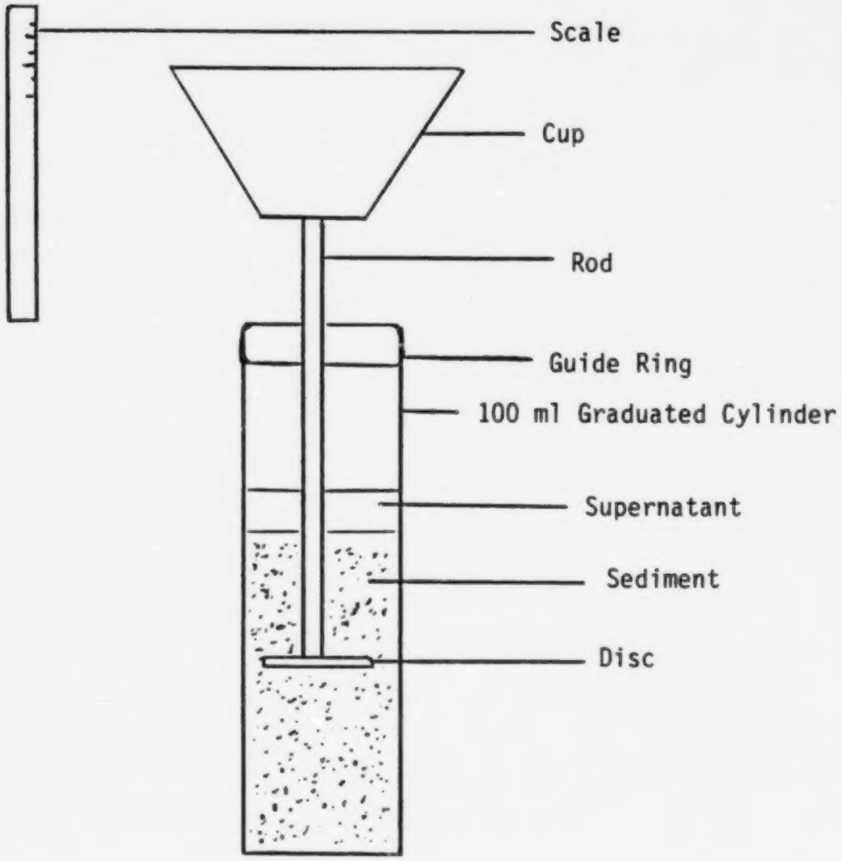

Scale
Cup
Rod
Guide Ring
100 ml Graduated Cylinder
Supernatant
Sediment
Disc

Figure 6.1 Modified rod penetrometer used in penetration tests of slurry sediments.

recorded. The cup was then placed on the end of the rod while the rod was held in place. It was then released and the timer started again. If there was no increase in penetration depth after 1 min the penetration depth was recorded. A known weight was then carefully added to the cup. This process was repeated with the addition of more and more weight until either the rod had reached the bottom of the sediment or the change in penetration depth was less than 1 mm, 3 min after adding a weight. In cases where the rod had not stopped moving after 1 min it was allowed to continue penetrating the sediment until it stopped or reached the bottom. The time required to penetrate the sediment completely was measured in cases where the rod alone was able to achieve complete penetration of the sediment.

After a penetration test was completed, redispersal of the sediment was attempted using the rod. A qualitative assessment of the sediment consistency was then made. Unfortunately, many of the slurries could not be redispersed. Consequently, penetration tests immediately after redispersal were only carried out on a few slurries.

6.2.6 Rheology Measurements

6.2.6.1 Apparatus

Slurry viscosities were measured with a Brookfield RVT rotational viscometer that was equipped with a small sample adapter. The small sample adapter allowed small sample volumes (8 ml) to be measured. It also provides a concentric cylinder geometry for which shear rates were well defined. This instrument could measure viscosities as high as 100,000 cP, at 8 different shear rates from 9.3 to 93 S^{-1}.

6.2.6.2 Procedure

After the rod penetration tests were completed, the slurries were redispersed. Slurries that could not be redispersed were discarded. An 8 ml sample of the freshly redispersed slurry was then introduced into the small sample adapter cup using a plastic, disposable syringe. The rotational bob was then carefully inserted into the small sample adapter cup and allowed to sink into the slurry sample. The viscosity of the sample was then measured as a function of shear rate from 9.3 S^{-1} to 93 S^{-1}. These measurements were carried out at room temperature (20 ± 2°C).

6.2.7 Contact Angle Measurements

Attempts to measure contact angles on powdered CANMET hydrocracked pitch by application of the Washburn-Rideal equation to measured wetting rates obtained for various liquids were unsuccessful. In order to obtain a value for the contact angle by this method, it is necessary to measure the wetting rates for a homologous series of n-alkanes (149). However, the pitch exhibited a significant solubility in these liquids. Consequently, meaningful wetting rates could not be obtained with these liquids.

7.0 EVALUATION OF CANMET HYDROCRACKED PITCH SLURRIES

7.1 Interpretation Of Penetration Data

Figure 7.1 shows a typical plot of the fractional penetration as a function of the total weight of the rod, cup and any weights added to the cup. The total weight will be referred to as the "rod loading" hereafter. The fractional penetration (FP) is defined in equation [7.1] and describes the fraction of the total length of the sediment column penetrated by the rod.

$$FP = \frac{L_p}{L_t} \qquad [7.1]$$

Where L_p is the distance from the top of the sediment column to the bottom of the disc that is attached to the rod and L_t is the total length of the sediment column.

The adjusted penetration area (A_{adj}) is shown as the shaded area in figure 7.1 and can be shown to be defined by equation [7.2].

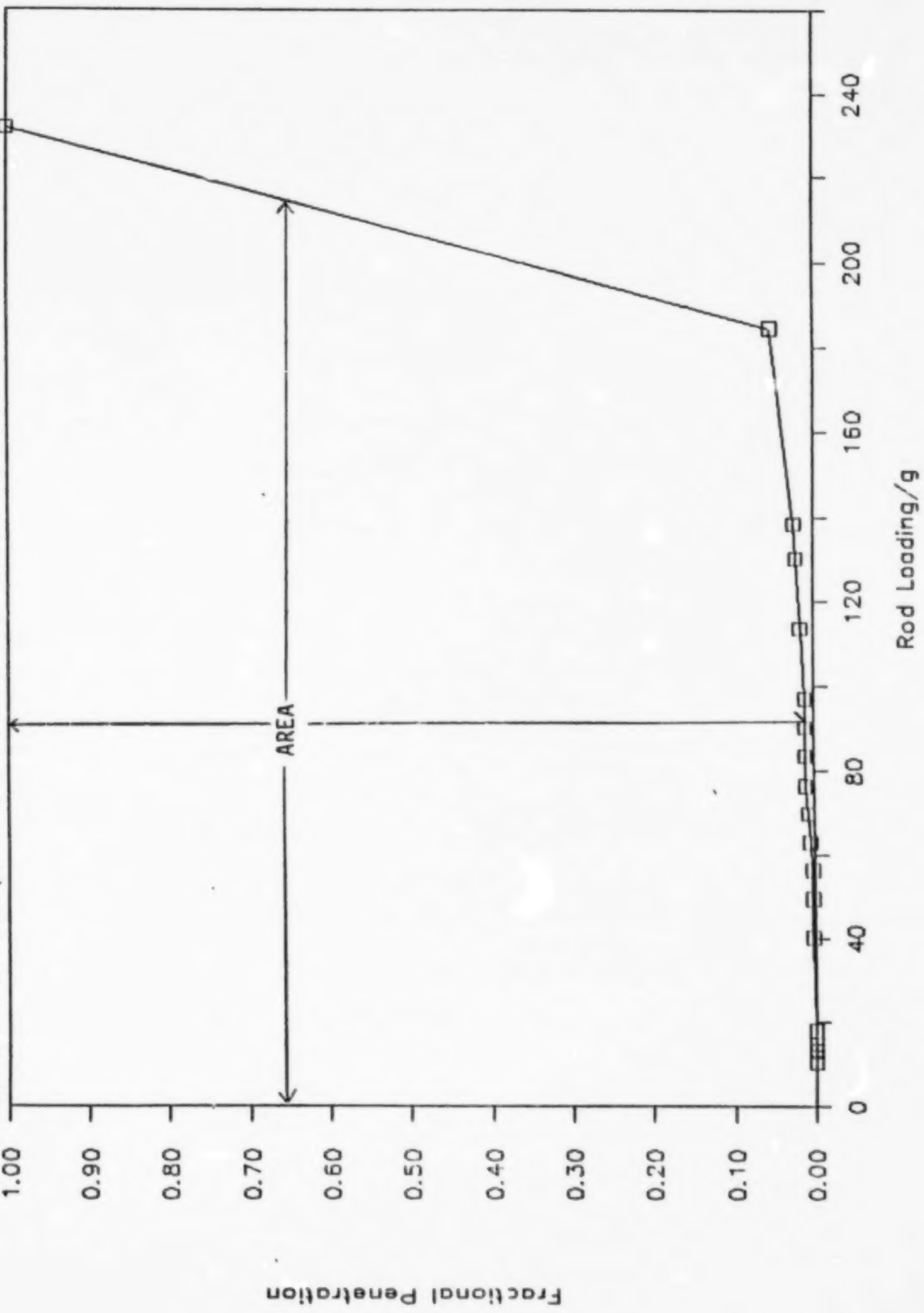


Figure 7.1 Fractional penetration as a function of rod loading for a slurry containing 50 wt% -325 mesh pitch and 0.10 wt% PLURONIC F-108.

$$A_{adj} = \frac{\int M \, dFP}{\int dLp} \qquad [7.2]$$

$$= \frac{1}{g} \, \frac{\int Mg \, dLp}{\int dLp}$$

Where M is the rod loading at any given point and g is the acceleration due to gravity. The integral term in the numerator of the second expression in equation [7.2] corresponds to the work done by the rod in penetrating the sediment (assuming that the effect of friction between the guide ring and the rod is negligible). Consequently, inspection of equation [7.2] indicates that A_{adj} is the average work required to penetrate 1 cm of the sediment (averaged over the length of the sediment bed that was actually penetrated) divided by the acceleration due to gravity. Clearly, low values of A_{adj} are desirable and high values are undesirable.

The definition of A_{adj} differs slightly from the definition of the penetration area (A) outlined in reference (148). In reference (148) the penetration area was defined as shown in equation [7.3].

$$A = \int M \, dFP \qquad [7.3]$$

$$= \frac{1}{g \, L_t} \int Mg \, dL_p$$

Clearly, $A_{adj} = A$ when the rod completely penetrates the sediment. Furthermore, inspection of equation [7.3] indicates that A can be interpreted in an identical fashion to that given above for A_{adj}, except that the work performed by gravity in penetrating the sediment is averaged over the entire length of the slurry sediment. In the present work, a large number of slurries yielded sediments which did not permit penetration of the entire sediment length. Therefore, it was both more appropriate and expedient to employ the concept of A_{adj} in the interpretation of the penetration data. The values of A used in this work were obtained by a numerical integration of equation [7.2] using the trapazoidal rule.

7.2 Effect Of Surfactants On Aqueous Slurries Of CANMET Hydrocracked Pitch

7.2.1 Introduction

In previous studies of aqueous oil sands coke slurries (148), it was reported that A (see equation [7.3]) was very sensitive to:

(1) surfactant concentration

(2) surfactant type

(3) stabilizer concentration

(4) stabilizer type

(5) solids concentration

(6) particle size distribution

(7) time elapsed since dispersal.

However, the present discussion will only be concerned with the effect of varying surfactant concentration.

In that work, values of A decreased with increasing surfactant concentration until it achieved a minimum value. Increasing the surfactant concentration above that which yielded the minimum value of A, caused A to increase. It was suggested that the minimum value of A corresponded to the optimum combination of fluidity and sedimentation stability. Moreover, it was also suggested that the concentration of surfactant that produced the minimum value of A was in fact the optimum concentration. It was proposed that the degree of particle flocculation in slurries containing the optimum concentration of surfactant was just sufficient to arrest particle settling at a point where the sediment was still loosely packed and easily redispersed without adversely affecting the slurry fluidity.

Slurries in which the surfactant concentration was below the optimum concentration exhibited excellent stability against sedimentation. However, these slurries also exhibited very high viscosities if the surfactant concentration was much below the optimum concentration. This was attributed to excessive particle flocculation.

As the surfactant concentration was increased the degree of particle flocculation and the viscosity of the slurries both decreased. Slurries in which the surfactant concentration exceeded the optimum concentration were extremely fluid. However, the sedimentation stability of these slurries decreased dramatically as the surfactant concentration increased. Such slurries yielded sediments that were increasingly dense and difficult to redisperse. It was suggested that the degree of flocculation in these slurries was too low to effectively inhibit particle settling. Consequently, particle settling could continue until sediments became extremely hard packed.

7.2.2 Effect Of Surfactant Concentration On Sediment Consistency

Tables 7.1, 7.2 and 7.3 contain the values of A_{adj} obtained as a function of surfactant concentration (for various surfactants) from aqueous slurries containing 50 wt%, -325 mesh pitch, 50 wt%, -200 mesh pitch and 60 wt%, -200 mesh pitch respectively. These tables also contain a qualitative assessment of the slurry consistency just after it was prepared. This assessment allows a distinction to be made between the case where the surfactant concentration is below the optimum concentration (characterized by high viscosity) and that where the surfactant concentration exceeds it (characterized by very low viscosity). In many cases, limited data in the area of the optimum concentration precludes distinguishing these two cases only on the basis of the A_{adj} values. These data are also shown graphically in figures 7.2 to 7.25.

Table 7.1 A_{adj} as a function of surfactant concentration for slurries containing 50 wt% -325 mesh CANMET hydrocracked pitch.

SURFACTANT		A_{adj}	INITIAL CONSISTENCY*
NAME	CONC. wt%	g	
NONE	0.00	HIGH	N.F.I.
PLURONIC F-108	0.10	193	V. THICK
	0.20	357	V. FLUID
	0.40	425	V. FLUID
	0.50	290	V. FLUID
	1.00	17	V. FLUID
TETRONIC 1508	0.10	HIGH	N.F.I.
	0.20	26	V. THICK
	0.30	249	V. FLUID
	0.40	26369	V. FLUID
	0.50	10938	V. FLUID
ANTAROX DM-970	0.20	12	V. THICK
	0.30	210	V. FLUID
	0.40	138	V. FLUID
	0.50	375	V. FLUID
LOMAR D	0.10	HIGH	N.F.I.
	0.20	503	V. THICK
	0.30	21078	V. FLUID
	0.40	32363	V. FLUID
FENOPON TK-32	0.20	HIGH	N.F.I.
	0.30	1609	V. THICK
	0.50	57	V. THICK
LIGNOSOL XD	0.10	0	FLUID
	0.30	0	V. FLUID
	0.50	44	V. FLUID
	1.00	218	V. FLUID
	5.00	1719	V. FLUID

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 7.1 A_{adj} as a function of surfactant concentration for slurries containing 50 wt% -325 mesh CANMET hydrocracked pitch (CONTINUED).

SURFACTANT		A_{adj}	INITIAL CONSISTENCY*
NAME	CONC. wt%	g	
LIGNOSOL TSD	0.10	0	FLUID
	0.20	0	V. FLUID
	0.30	0	V. FLUID
	0.50	117	V. FLUID
	1.00	369	V. FLUID
	5.00	317	V. FLUID
MARASPERSE CBX-2	0.10	0	V. FLUID
	0.20	18	V. FLUID
	0.30	100	V. FLUID
	0.40	244	V. FLUID
	0.50	1920	V. FLUID
	1.00	11732	V. FLUID
	5.00	19240	V. FLUID
MARASPERSE CBOS-3	0.10	105	V. FLUID
	0.20	365	V. FLUID
	0.30	402	V. FLUID
	0.40	227	V. FLUID
	0.50	102	V. FLUID

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 7.2 A_{adj} as a function of surfactant concentration for slurries containing 50 wt% -200 mesh CANMET hydrocracked pitch.

SURFACTANT NAME	CONC. wt%	A_{adj} g	INITIAL CONSISTENCY*
NONE	0.00	HIGH	N.F.I.
PLURONIC F-108	0.10	11	V. FLUID
	0.20	173	V. FLUID
	0.30	175	V. FLUID
	0.40	196	V. FLUID
	0.50	184	V. FLUID
TETRONIC 1508	0.10	32	V. THICK
	0.20	48	V. THICK
	0.30	92	V. FLUID
	0.40	152	V. FLUID
ANTAROX DM-970	0.10	105	V. THICK
	0.20	142	V. THICK
	0.30	261	V. FLUID
	0.40	506	V. FLUID
LOMAR D	0.10	HIGH	N.F.I.
	0.20	3024	V. THICK
	0.30	3638	V. FLUID
	0.40	4950	V. FLUID
FENOPON TK-32	0.10	HIGH	N.F.I.
	0.20	HIGH	N.F.I.
	0.30	301	V. THICK
	0.40	152	V. THICK
	0.50	21	THICK
	0.70	8	THICK
LIGNOSOL XD	0.10	0	FLUID
	0.20	14205	V. FLUID
	0.30	13664	V. FLUID
	0.40	556	V. FLUID
	0.50	368	V. FLUID

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 7.2 A_{adj} as a function of surfactant concentration for slurries containing 50 wt% -200 mesh CANMET hydrocracked pitch (CONTINUED).

SURFACTANT		A_{adj}	INITIAL CONSISTENCY*
NAME	CONC. wt%	g	
LIGNOSOL TSD	0.10	481	V. FLUID
	0.20	59	V. FLUID
	0.30	224	V. FLUID
	0.40	660	V. FLUID
MARASPERSE CBX-2	0.10	2	FLUID
	0.20	316841	V. FLUID
	0.30	32794	V. FLUID
	0.40	117171	V. FLUID
MARASPERSE CBOS-3	0.10	HIGH	N.F.I
	0.20	116494	V. FLUID
	0.30	6947	V. FLUID
	0.40	175878	V. FLUID
LIGNOSOL BD	INSUFFICIENT PITCH		

*N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 7.3 A_{adj} as a function of surfactant concentration for slurries containing 60 wt% -200 mesh CANMET hydrocracked pitch.

SURFACTANT NAME	CONC. wt%	A_{adj} g	INITIAL CONSISTENCY*
PLURONIC F-108	0.10-0.90	HIGH	N.F.I
	1.80	HIGH	N.F.I.
	1.90	6	THICK
	2.00	6	THICK
	2.10	10	THICK
TETRONIC 1508	0.80-1.00	HIGH	N.F.I
	1.80	HIGH	N.F.I.
	1.90	133	V. THICK
	2.00	94	V. FLUID
	2.10	220	V. FLUID
ANTAROX DM-970	1.80	HIGH	N.F.I.
	1.90	HIGH	N.F.I.
	2.00	HIGH	N.F.I.
	2.20	HIGH	N.F.I.
	2.60	HIGH	N.F.I.
	3.00	HIGH	N.F.I.
LOMAR D	0.70	251	V. THICK
	0.80	64	FLUID
	0.90	110	V. FLUID
	1.00	262	V. FLUID
FENOPON TK-32	1.80	HIGH	N.F.I.
	1.90	HIGH	N.F.I.
	2.00	HIGH	N.F.I.
	2.20	HIGH	N.F.I.
	2.60	HIGH	N.F.I.
	3.00	HIGH	N.F.I.
LIGNOSOL XD	0.70	1771	V. THICK
	0.80	382	V. THICK
	0.90	73	V. FLUID
	1.00	379	V. FLUID

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 7.3 A_{adj} as a function of surfactant concentration for slurries containing 60 wt% -200 mesh CANMET hydrocracked pitch (CONTINUED).

SURFACTANT		A_{adj}	INITIAL CONSISTENCY*
NAME	CONC. wt%	g	
LIGNOSOL TSD	0.70	3863	V. THICK
	0.80	790	V. THICK
	0.90	17	V. FLUID
	1.00	255	V. FLUID
	1.10	276	V. FLUID
MARASPERSE CBX-2	0.70	1333	V. THICK
	0.80	243	V. THICK
	0.90	285	V. FLUID
	1.00	796	V. FLUID
MARASPERSE CBOS-3	0.70	358	V. THICK
	0.80	117	V. THICK
	0.90	312	V. FLUID
	1.00	1389	V. FLUID
LIGNOSOL BD	INSUFFICIENT PITCH		

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Figure 7.2 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and PLURONIC F-108.

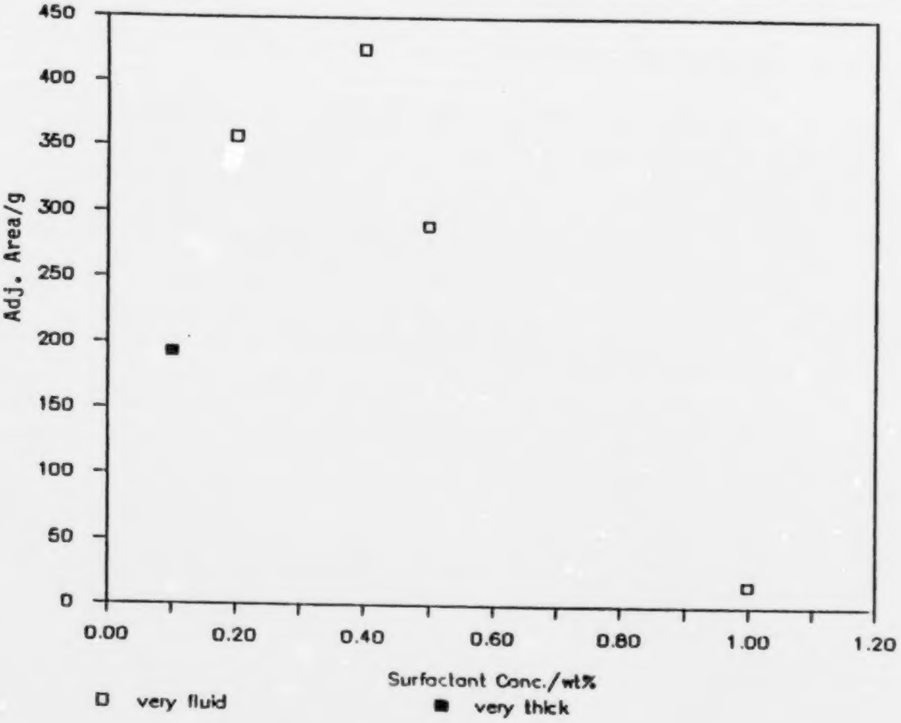


Figure 7.3 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and TETRONIC 1508.

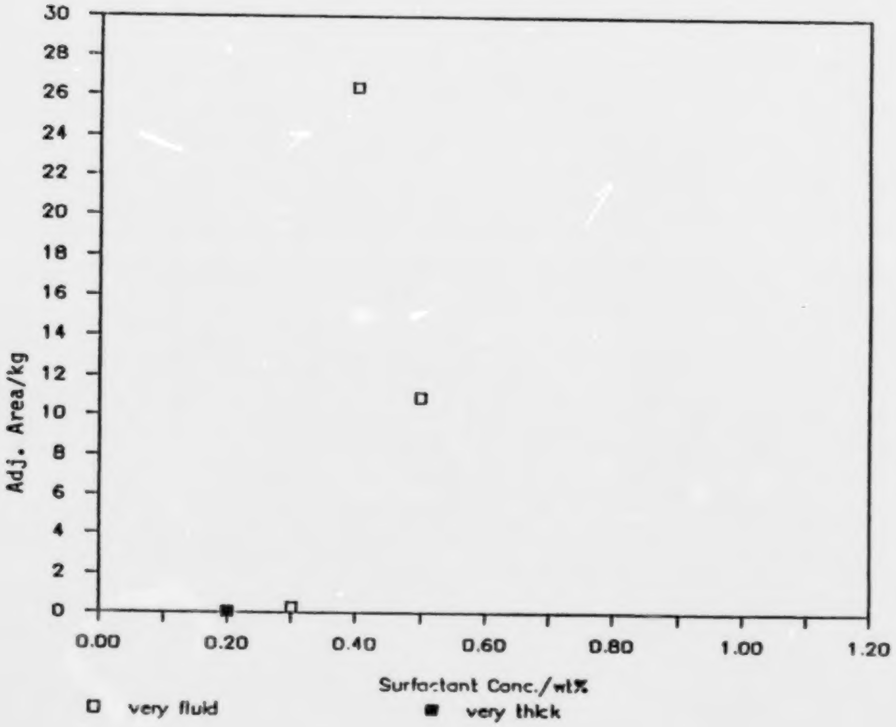


Figure 7.4 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and ANTAROX DM-970.

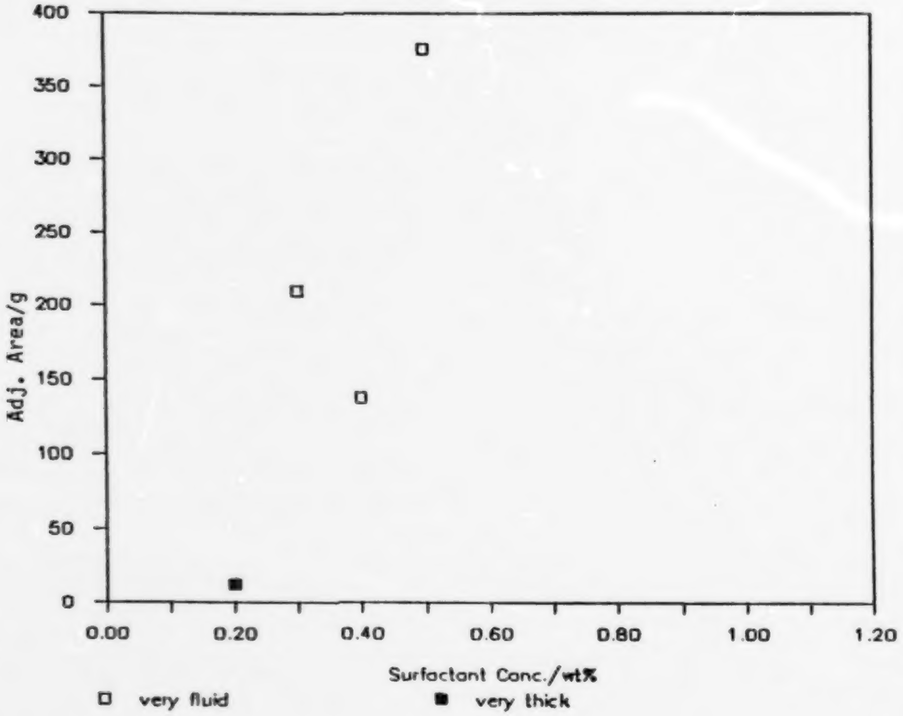


Figure 7.5 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and LOMAR D.

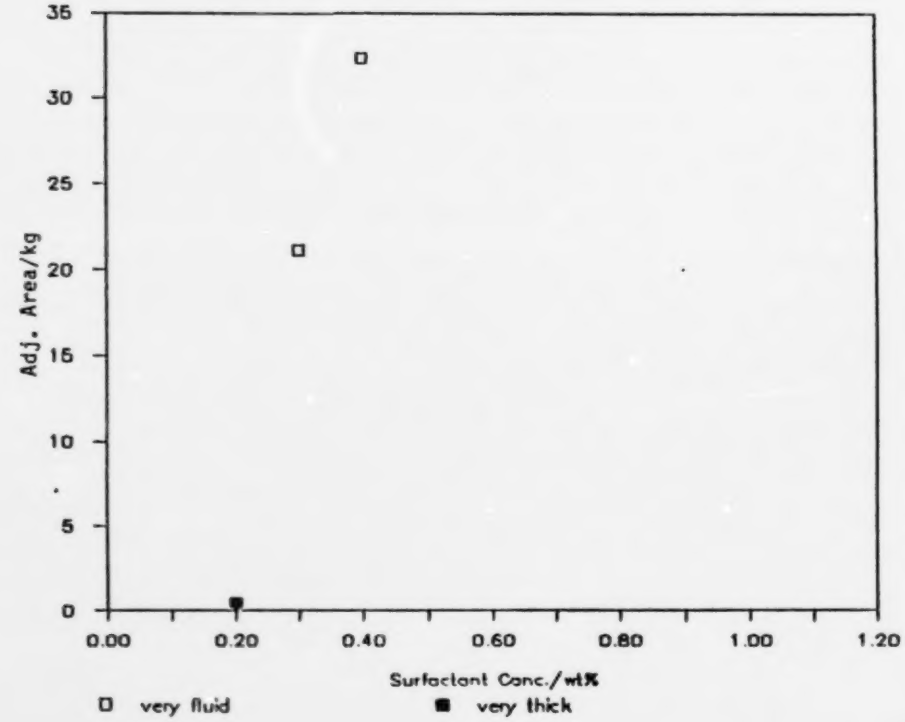


Figure 7.6 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and LIGNOSOL XD.

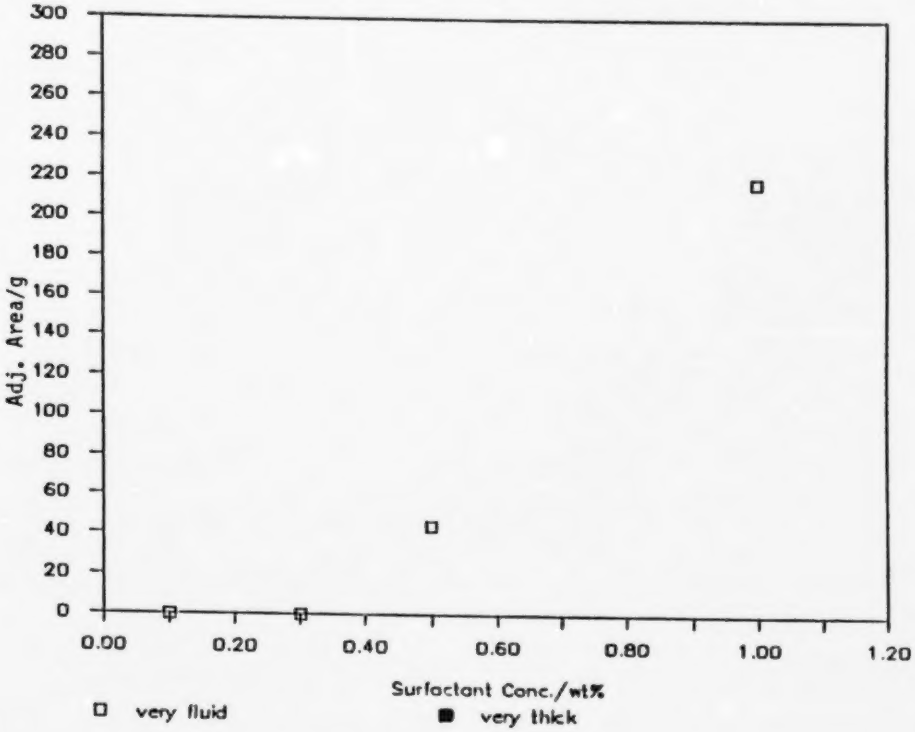


Figure 7.7 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and LIGNOSOL TSD.

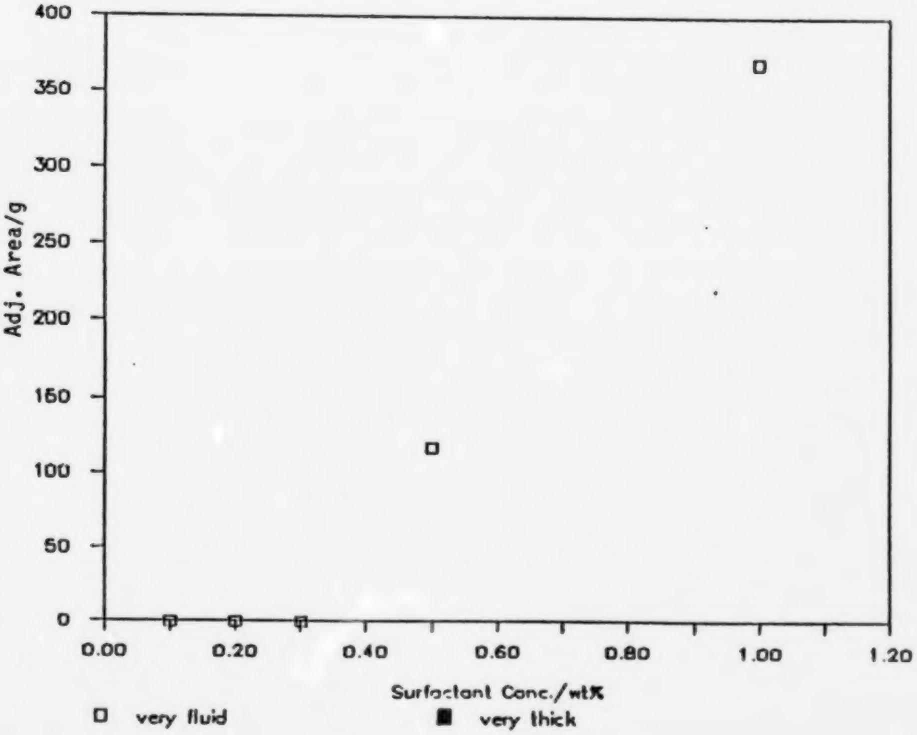


Figure 7.8 Adjusted area as a function of surfactant concentration forslurries containing 50 wt% -325 mesh pitch and MARASPERSE CBX-2.

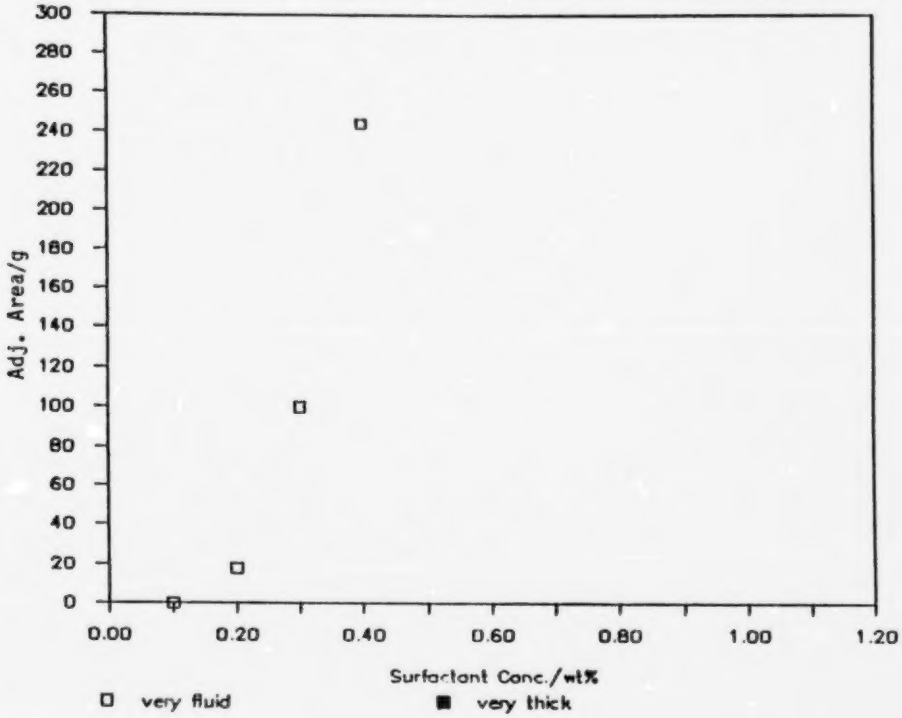


Figure 7.9 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -325 mesh pitch and MARASPERSE CBOS-3.

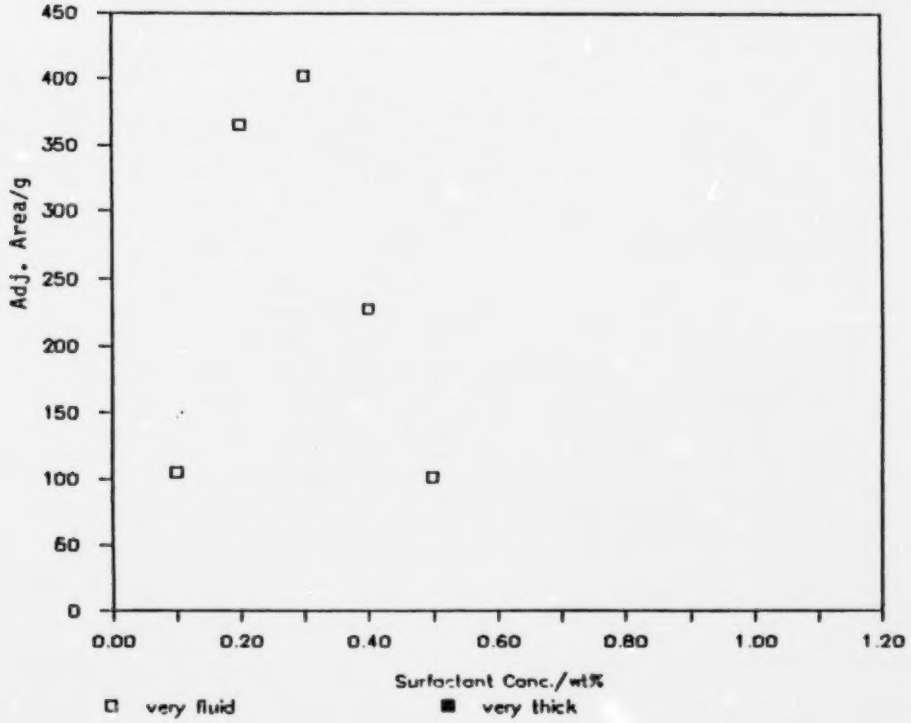


Figure 7.10 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and PLURONIC F-108.

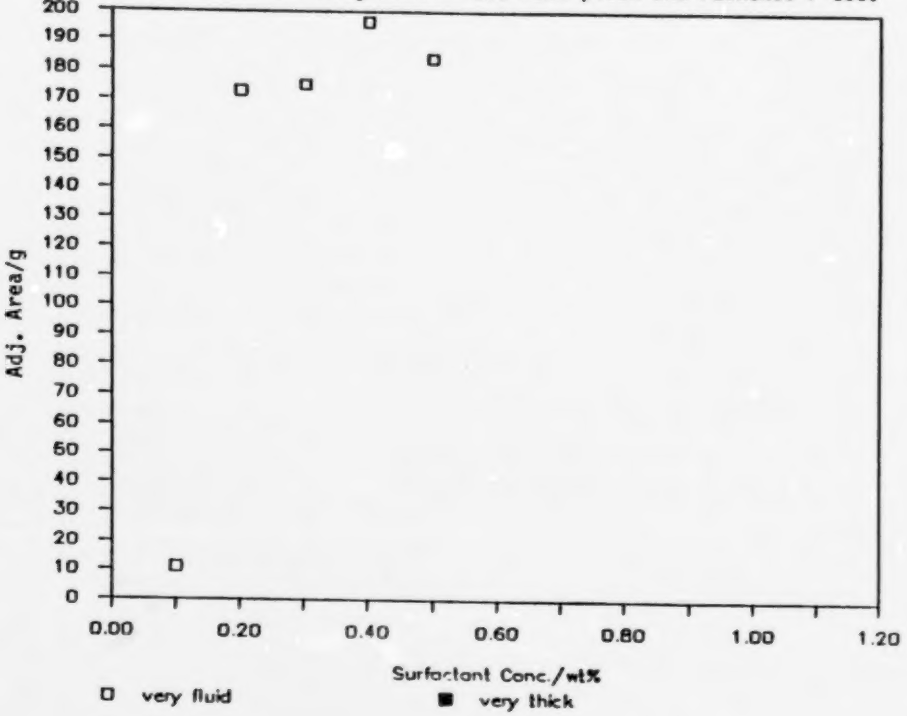


Figure 7.11 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and TETRONIC 1508.

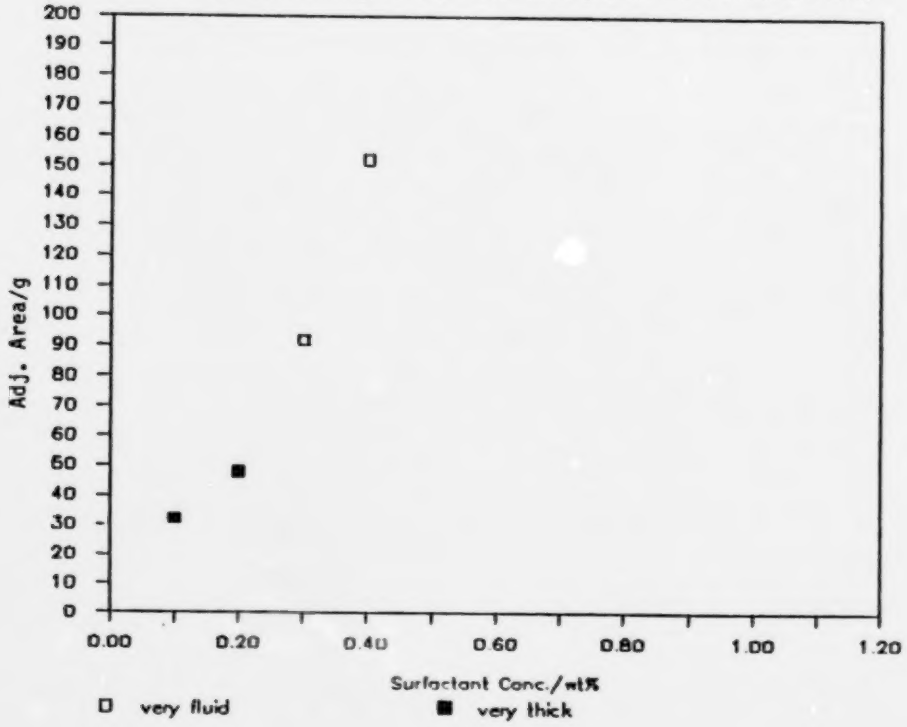


Figure 7.12 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and ANTAROX DM-970.

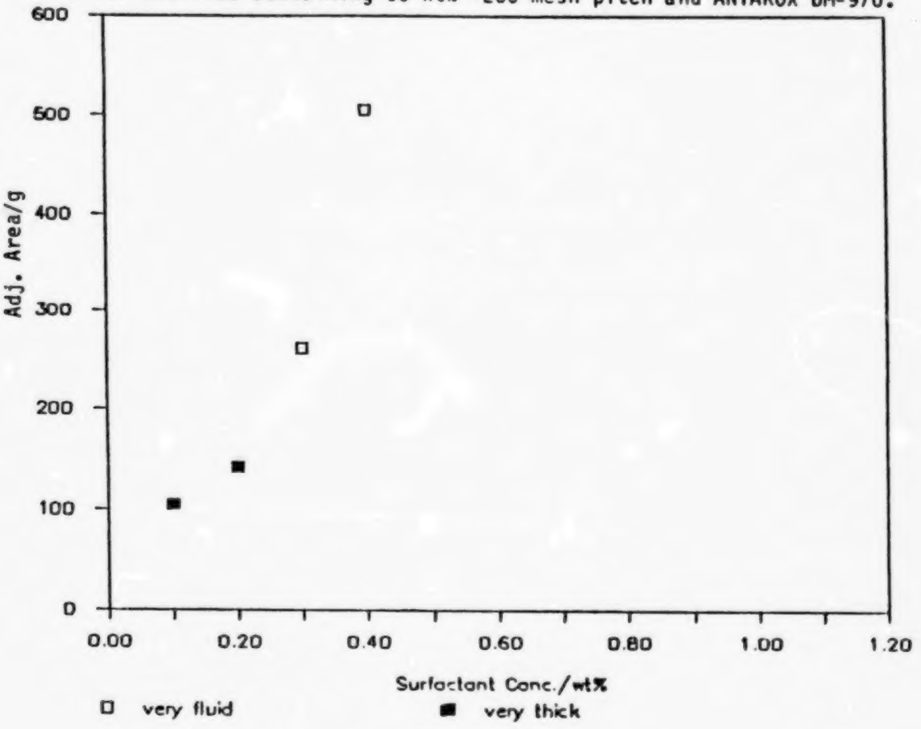


Figure 7.13 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and LOMAR D.

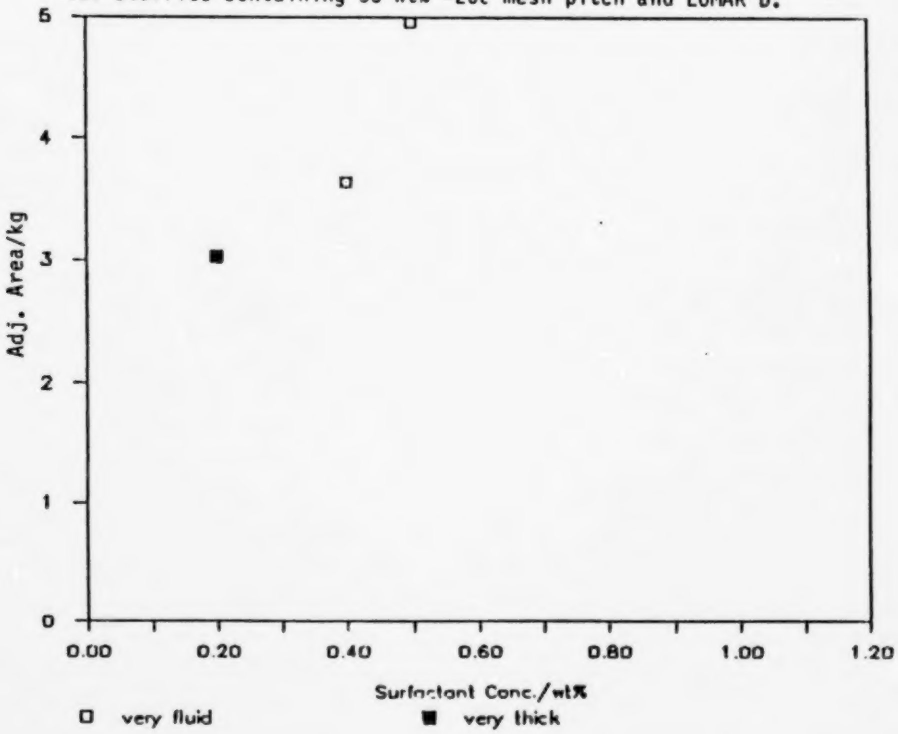


Figure 7.14 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and FENOPON TK-32.

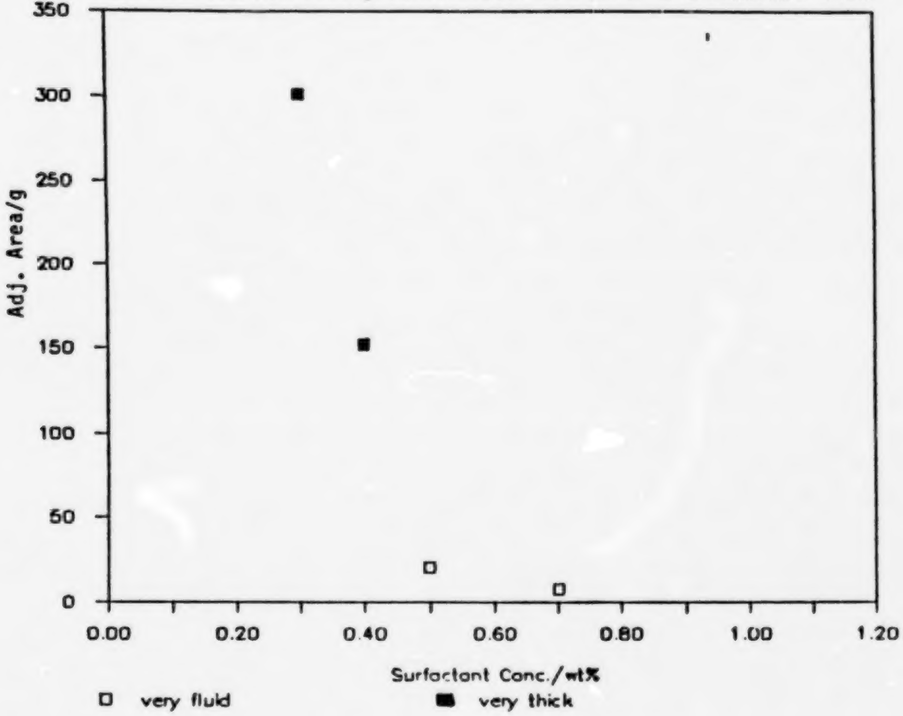


Figure 7.15 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and LIGNOSOL XD.

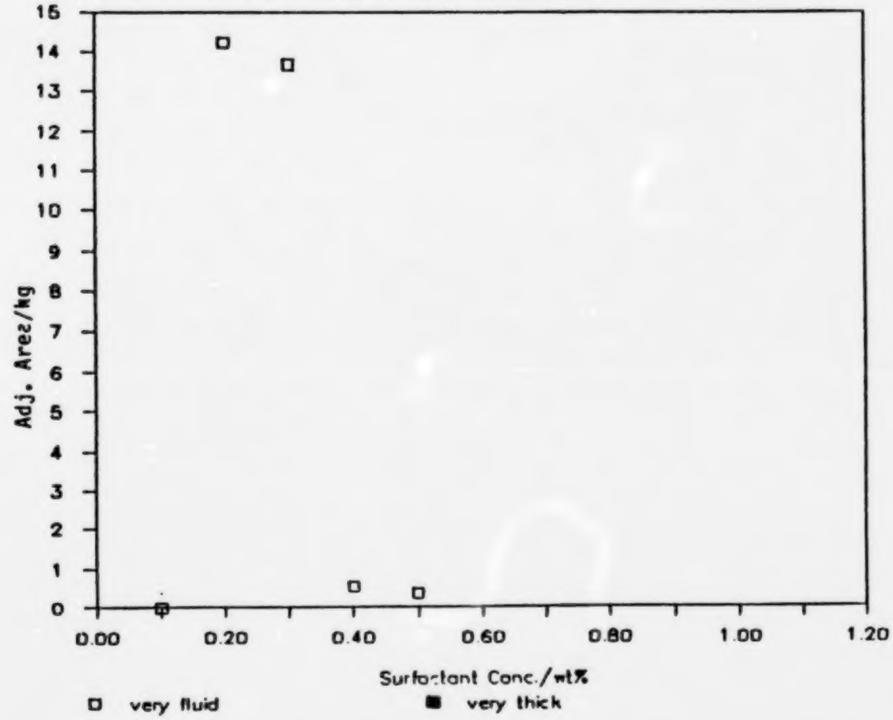


Figure 7.16 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and LIGNOSOL TSD.

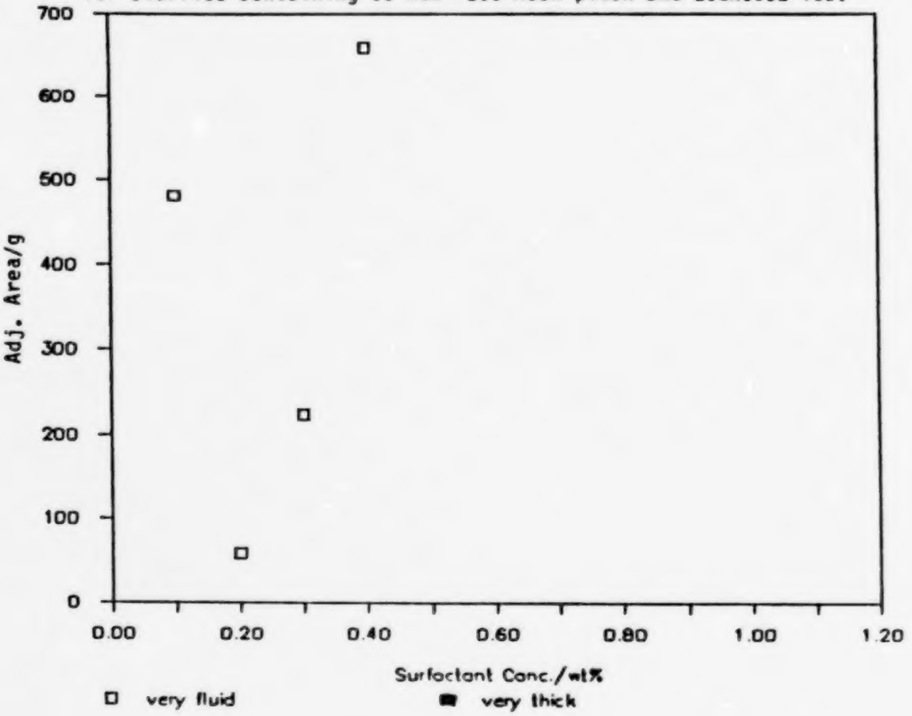


Figure 7.17 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and MARASPERSE CBX-2.

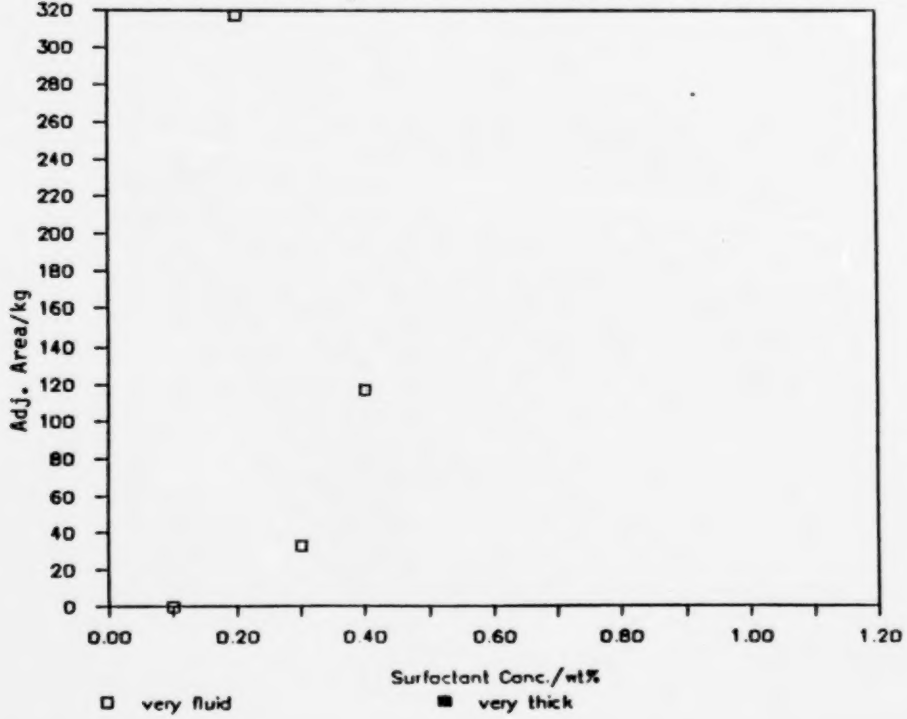


Figure 7.18 Adjusted area as a function of surfactant concentration for slurries containing 50 wt% -200 mesh pitch and MARASPERSE CBOS-3.

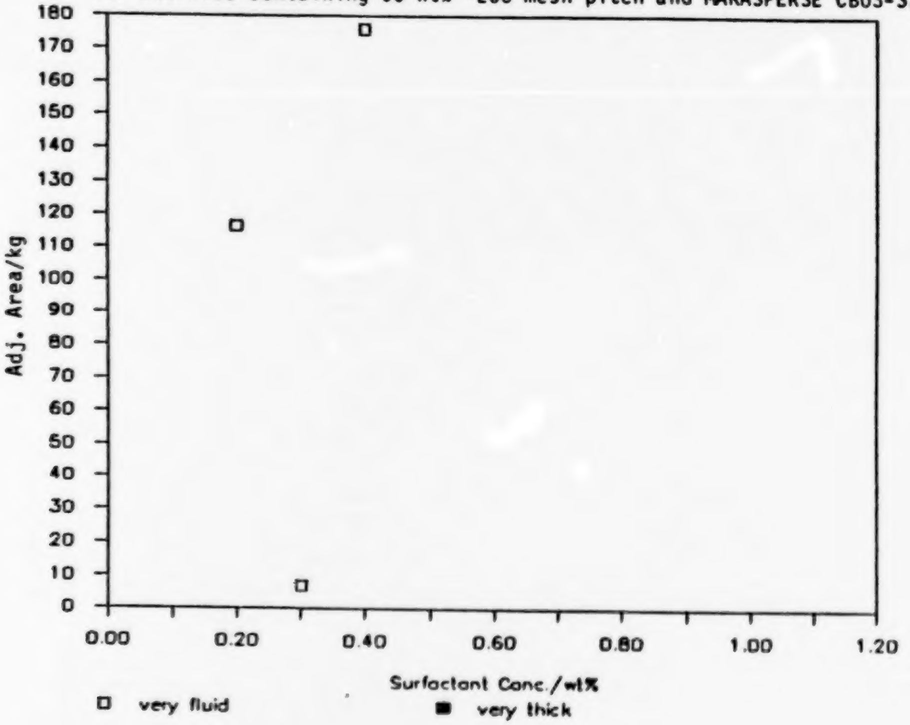


Figure 7.19 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and PLURONIC F-108.

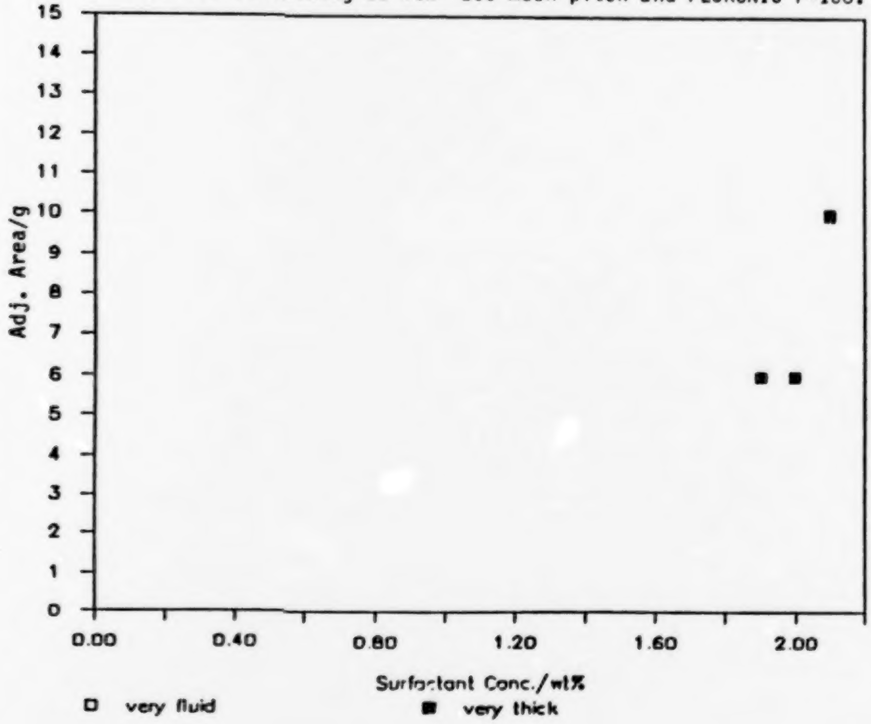


Figure 7.20 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and TETRONIC 1508.

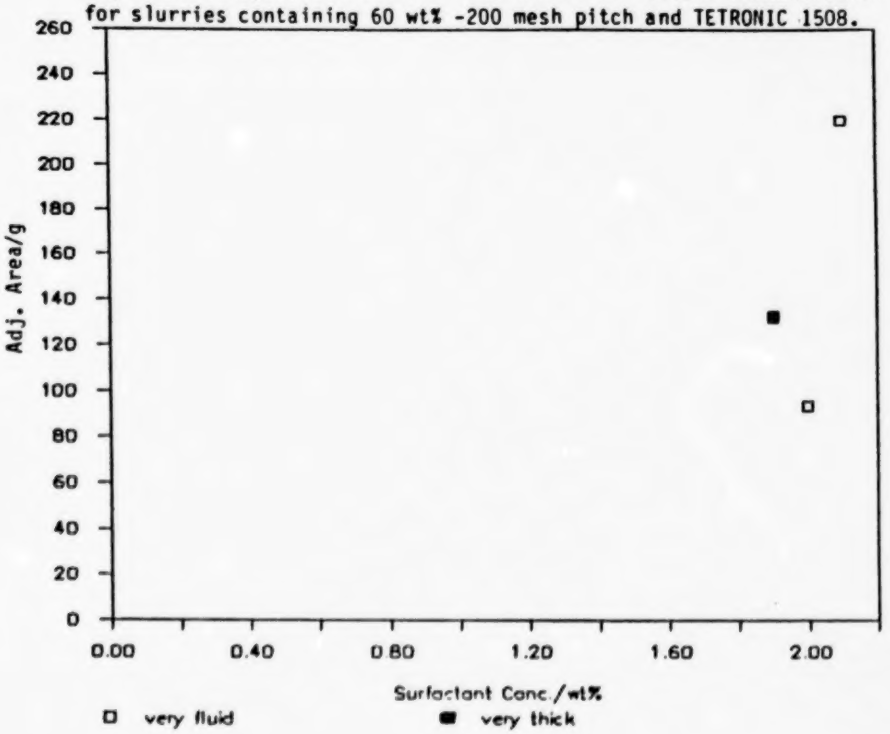


Figure 7.21 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and LOMAR D.

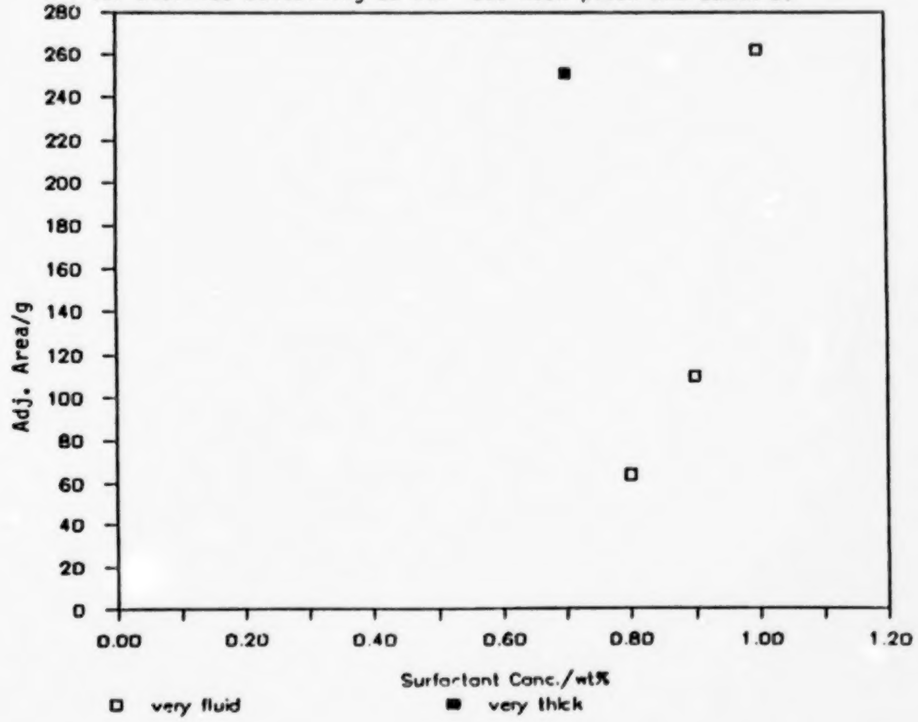


Figure 7.22 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and LIGNOSOL XD.

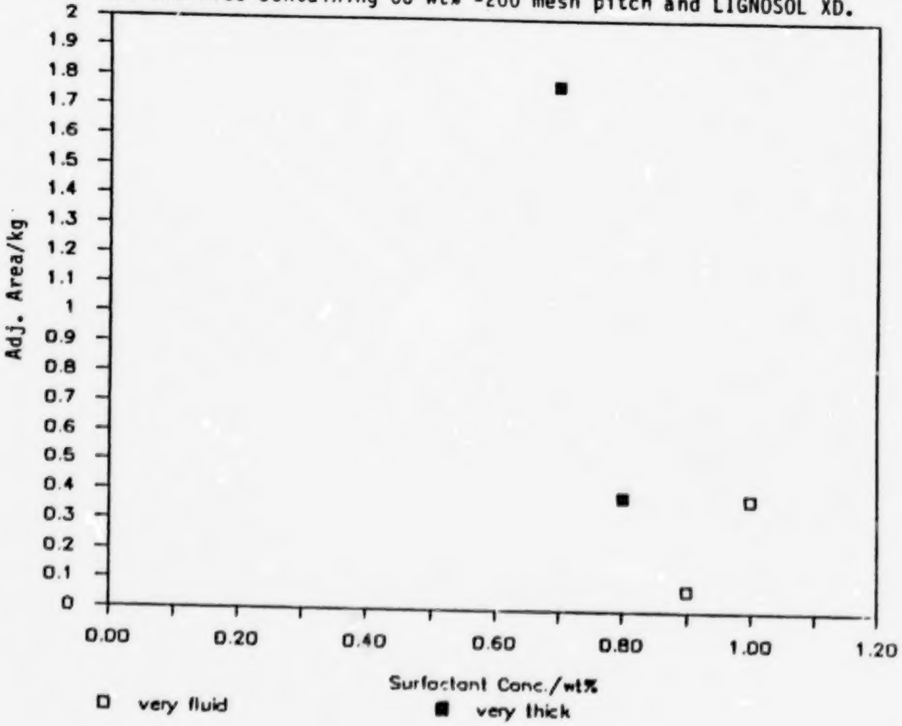


Figure 7.23 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and LIGNOSOL TSD.

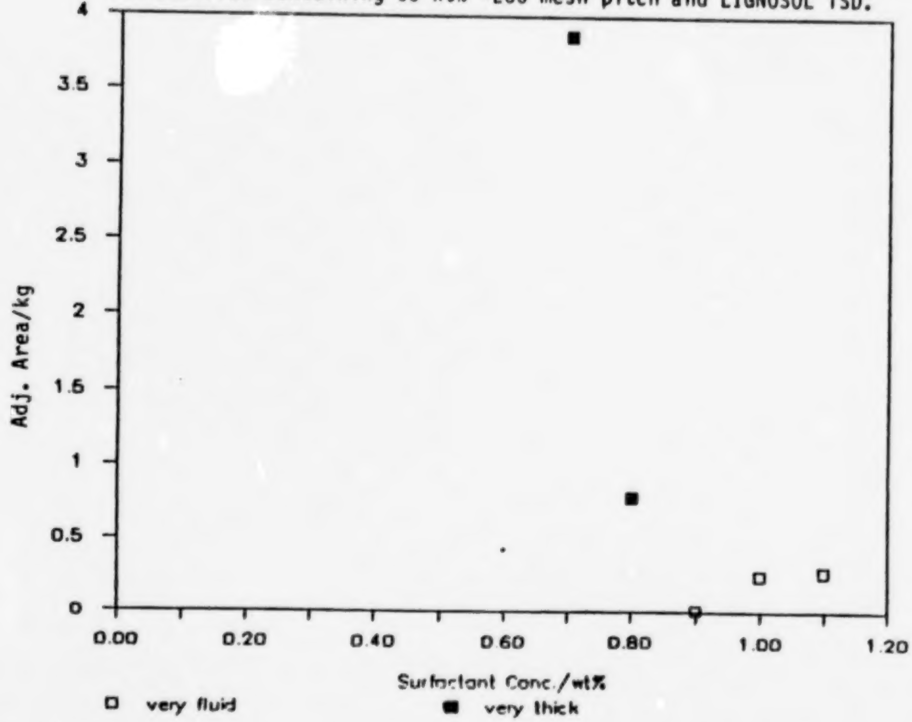


Figure 7.24 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and MARASPERSE CBX-2.

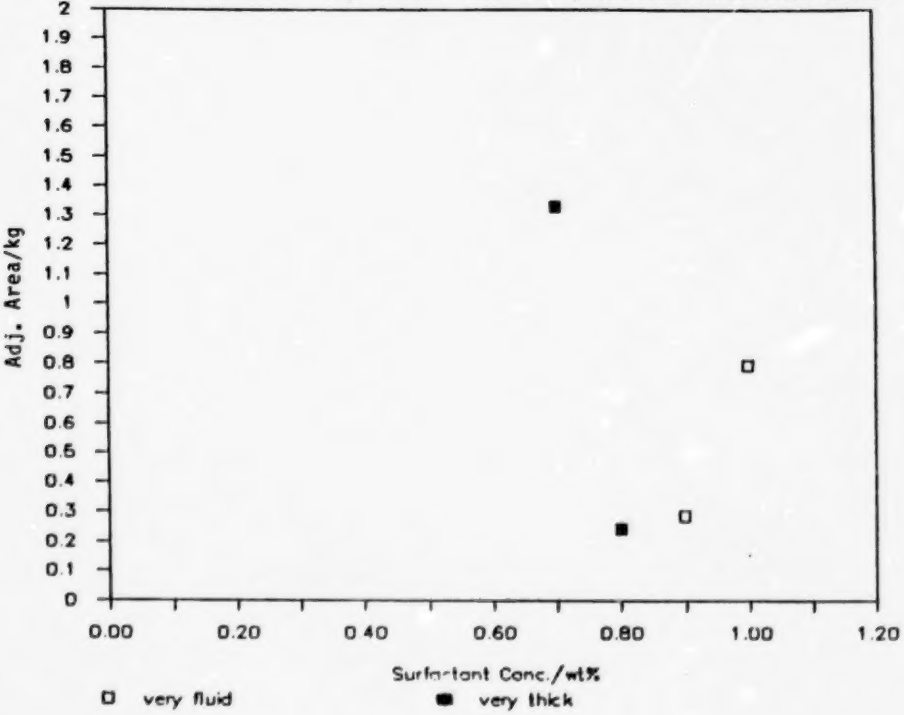
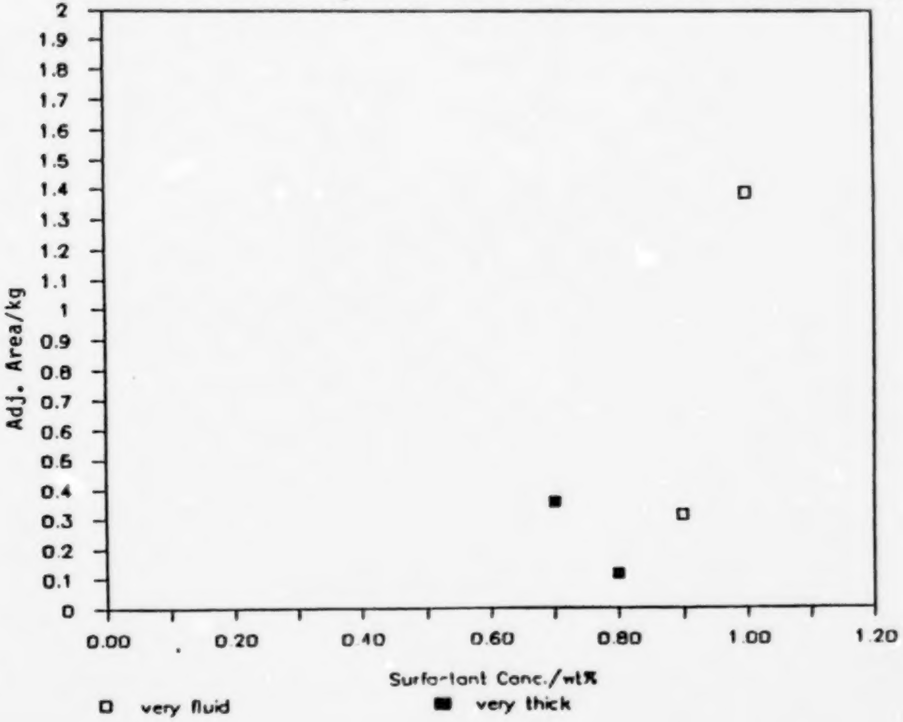


Figure 7.25 Adjusted area as a function of surfactant concentration for slurries containing 60 wt% -200 mesh pitch and MARASPERSE CBOS-3.



It is clear from the data shown in figures 7.2 to 7.25 that, in many cases (see figures: 7.3, 7.5-7.9, 7.11-7.14, 7.20-7.25), A_{adj} shows a dependence on surfactant concentration that is similar to that described above for A. This is not surprising given the similarity in the definitions of A and A_{adj}. In other cases the similarity is not immediately obvious. This is attributable to the sparsity of the data in the neighborhood of the optimum surfactant concentration. It is further complicated by the surprisingly narrow concentration range (as little as 0.10 wt%) over which the transition from insufficient to excessive amounts of surfactant occurs.

In some cases A_{adj} also exhibits a maximum and then decreases with further increases in surfactant concentration (see figures 7.2, 7.3, 7.9, 7.15). It is likely, at least in the instances where long chain nonionic surfactants were employed, that this can be attributed to increased viscosity of the liquid medium. It is well known that the viscosity of a polymer solution can increase significantly when the solute polymer concentration increases. In other cases (see figures 7.4, 7.16-7.18), there is some scatter of A_{adj} values as the surfactant concentration increases. This is likely the result of the extremely hard packed nature of the slurry sediments in these cases. More specifically, even when the rod loading was very high, penetration of such sediments was minimal. Consequently, the uncertainty on the fractional penetration and therefore on the value of A_{adj} is very large. Therefore scatter is not unexpected when A_{adj} values are very high (above 100 g).

It was not possible to prepare slurries containing 50 wt% of either PSD without adding a surfactant. Thus, the volume concentration of the pitch in such slurries exceeds the critical solids volume concentration (CSVC) for the system (see section 3.1). It is well known that the CSVC of a system can be increased by the addition of suitable quantities of surfactants. This is attributable to the more efficient particle packing that is possible as the degree of particle flocculation is reduced.

7.2.3 Effect Of Varying Surfactant On Sediment Consistency

The data provided by this work permit the establishment of upper and lower limits for the range of surfactant concentrations in which the optimum concentration should be found. Tables 7.4-7.5 contain the limits for the surfactant concentration range that is likely to contain the optimum concentration of surfactant for slurries containing 50 wt% -325 mesh pitch, 50 wt% -200 mesh pitch and 60 wt% -200 mesh pitch respectively. The data shown in tables 7.4-7.6 indicate that the PLURONIC F-108 is the most effective nonionic surfactant for slurries containing 50 wt% of either PSD while TETRONIC 1508 is the most effective nonionic surfactant for slurries containing 60 wt% -200 mesh pitch.

The lignosulphonates (LIGNOSOL XD, LIGNOSOL TSD, MARASPERSE CBX-2 and

Table 7.4 Range in which optimum surfactant concentration is likely to be found for slurries containing 50 wt% -325 mesh CANMET hydrocracked pitch.

SURFACTANT	RANGE wt%
PLURONIC F-108	0.10-0.20
TETRONIC 1508	0.20-0.30
ANTAROX DM970	0.20-0.30
LOMAR D	0.20-0.30
FENOPON TK-32	0.50
LIGNOSOL XD	0.00-0.50
LIGNOSOL TSD	0.00-0.50
MARASPERSE CBX-2	0.00-0.20
MARASPERSE CBOS-3	0.00-0.10

Table 7.5 Range in which optimum surfactant concentration is likely to be found for slurries containing 50 wt% -200 mesh CANMET hydrocracked pitch.

SURFACTANT	RANGE wt%
PLURONIC F-108	0.00-0.10
TETRONIC 1508	0.20-0.30
ANTAROX DM970	0.20-0.30
LOMAR D	0.20-0.30
FENOPON TK-32	0.70
LIGNOSOL XD	0.00-0.20
LIGNOSOL TSD	0.00-0.10
MARASPERSE CBX-2	0.00-0.10
MARASPERSE CBOS-3	0.00-0.20

Table 7.6 Range in which optimum surfactant concentration is likely to be found for slurries containing 60 wt% -200 mesh CANMET hydrocracked pitch.

SURFACTANT	RANGE wt%
PLURONIC F-108	2.10
TETRONIC 1508	2.00-2.10
ANTAROX DM970	3.00
LOMAR D	0.70-0.80
FENOPON TK-32	0.70
LIGNOSOL XD	0.80-0.90
LIGNOSOL TSD	0.80-0.90
MARASPERSE CBX-2	0.80-0.90
MARASPERSE CBOS-3	0.80-0.90

MARASPERSE CBOS-3) were all extremely effective for slurries containing 50 wt% of either PSD and 60 wt% of the -200 mesh pitch. In the slurries containing 60 wt% -200 mesh pitch, the lignosulphonates effectively dispersed the pitch at concentrations (about 0.9 wt%) that were less than half that required by the more expensive nonionic surfactants (greater than 2.10 wt%). Furthermore, it was possible to prepare slurries containing 50 wt% of either PSD, that were both extremely fluid and highly stable, using concentrations as low as 0.10 wt% of either of the LIGNOSOL lignosulphonates or MARASPERSE CBX-2.

In slurries containing 50 wt% of either PSD, the LOMAR D performed as well as the nonionic surfactants (with the exception of PLURONIC F-108). However, it was as effective as the lignosulphonates in the slurries containing 60 wt% of the -200 mesh pitch. The FENOPON TK-32 was the least effective of any surfactant employed in this work. Slurries that contained 50 wt% of either PSD were still highly flocculated at concentrations as high as 0.50 wt%. It was not possible to produce a slurry containing 60 wt% -200 mesh pitch in which all of the pitch was incorporated, even though the concentration was as high as 3.0 wt%

7.3 Effect Of Solids Concentration On Sediment Consistency

The data contained in tables 7.5 and 7.6 indicate that much more surfactant is required to significantly reduce the degree of particle flocculation in slurries containing 60 wt% -200 mesh pitch than in 50 wt%

-200 mesh pitch. For example a concentration of 0.10 wt% of PLURONIC F-108 is sufficient to virtually eliminate particle flocculation in a slurry containing 50 wt% -200 mesh pitch. However, a slurry containing 2.10 wt% of the same surfactant and 60 wt% -200 mesh pitch is highly flocculated. Similar behavior was observed with each of the other surfactants employed in this work. It is not unexpected that more surfactant would be required to achieve a given degree of dispersal in a more concentrated slurry than would be required in a less concentrated slurry since there are more particles in closer proximity to each other in the former case than in the latter case.

7.4 Effect Of Particle Size Distribution On Sediment Consistency

Intuitively, it would be expected that the optimum concentration of surfactant for a slurry would increase as the average particle size decreased. This would be attributed to a combination of two phenomena. In the first place coarser particles would require more flocculation to prevent them from settling out than would finer particles. Secondly, for a given concentration of surfactant, the degree of flocculation should be lower in a slurry containing coarser particles. This would result from the lower total surface area in such a slurry. Thus, a smaller amount of surfactant would be required to cover the particle surfaces and inhibit flocculation. The data listed in tables 7.4 and 7.5 indicate that the optimum concentrations of some surfactants occur in a lower concentration range for slurries containing 50 wt% -200 mesh pitch than is the case for the slurries that contain 50 wt% -325 mesh pitch. However, in most cases there is little difference between the two PSDs.

7.5 Slurry Rheology

The viscosities (at 9.3 S^{-1} and 93 S^{-1}) of slurries containing 50 wt% -325 mesh pitch, 50 wt% -200 mesh pitch and 60 wt% -200 mesh pitch are given in tables 7.7, 7.8 and 7.9 respectively. It is clear from the data contained in these tables that the presence of surfactants can greatly reduce the viscosities of aqueous pitch slurries. In general, the viscosities at both shear rates decline sharply, from values greater than 100,000 cP to values in the range of 11-50 cP, as the surfactant concentration increases. Once the viscosities reach values in the 11-50 cP range, they show relatively little dependence on the surfactant concentration. Such behavior can be attributed to the effect of the surfactant on particle flocculation. Initially the system is highly flocculated and the viscosity is very high. As the surfactant concentration is increased, the degree of flocculation and the slurry viscosity both decrease. Eventually, the system will be completely deflocculated and adding surfactant will have little effect.

All of the surfactants examined in this work, with the exception of the FENOPON TK-32, effectively reduced the viscosities of the slurries containing 50 wt% of either PSD. However, the lignosulphonates were

Table 7.7 Viscosity as a function of surfactant concentration for slurries containing 50 wt% -325 mesh CANMET hydrocracked pitch.

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	9.3 S^{-1} cP	93 S^{-1} cP
NONE	0.00	N.F.I.	N.F.I
PLURONIC F-108	0.10	100000	100000
	0.20	N.R.	N.R
	0.40	N.R.	N.R.
	0.50	N.R.	N.R.
	1.00	20.0	16.6
TETRONIC 1508	0.10	N.F.I.	N.F.I.
	0.20	3750.0	147.0
	0.30	16.3	11.5
	0.40	11.3	12.5
	0.50	17.5	12.1
ANTAROX DM-970	0.20	2550.0	77.0
	0.30	17.5	12.1
	0.40	20.0	13.3
	0.50	17.5	14.3
LOMAR D	0.10	N.F.I.	N.F.I.
	0.20	22.5	27.4
	0.30	N.R.	N.R.
	0.40	N.R.	N.R.
FENOPON TK-32	0.20	N.F.I.	N.F.I.
	0.30	100000	100000
	0.50	100000	100000
LIGNOSOL XD	0.10	50.1	31.8
	0.30	15.0	15.0
	0.50	12.5	12.3
	1.00	14.4	14.2
	5.00	27.5	20.0

* N.F.I.: PITCH NOT FULLY INCORPORATED.
N.R.: NOT REDISPERSABLE.

Table 7.7 Viscosity as a function of surfactant concentration for slurries containing 50 wt% -325 mesh CANMET hydrocracked pitch (CONTINUED).

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	9.3 S^{-1} cP	93 S^{-1} cP
LIGNOSOL TSD	0.10	120.0	37.8
	0.20	15.0	15.5
	0.30	17.5	14.5
	0.50	12.5	12.3
	1.00	15.0	13.0
	5.00	40.0	20.0
MARASPERSE CBX-2	0.10	100.0	30.0
	0.20	15.0	9.5
	0.30	N.R.	N.R.
	0.40	N.R.	N.R.
	0.50	N.R.	N.R.
	1.00	N.R.	N.R.
	5.00	N.R.	N.R.
MARASPERSE CBOS-3	0.10	N.R.	N.R.
	0.20	N.R.	N.R.
	0.30	N.R.	N.R.
	0.40	N.R.	N.R.
	0.50	N.R.	N.R.

* N.F.I.: PITCH NOT FULLY INCORPORATED.
N.R.: NOT REDISPERSABLE.

Table 7.8 Viscosity as a function of surfactant concentration for slurries containing 50 wt% -200 mesh CANMET hydrocracked pitch.

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	9.3 S^{-1} cP	93 S^{-1} cP
NONE	0.00	N.F.I.	N.F.I.
PLURONIC F-108	0.10	50.0	63.9
	0.20	47.5	30.0
	0.30	45.0	29.2
	0.40	14.0	13.2
	0.50	14.0	15.0
TETRONIC 1508	0.10	100.0	72.2
	0.20	100.0	51.1
	0.30	13.8	11.3
	0.40	13.8	12.6
ANTAROX DM-970	0.10	100000	100000
	0.20	100000	100000
	0.30	13.8	12.3
	0.40	13.8	17.5
LOMAR D	0.10	N.F.I	N.F.I.
	0.20	13.8	15.0
	0.30	N.R.	N.R.
	0.40	N.R.	N.R.
FENOPON TK-32	0.10	N.F.I.	N.F.I.
	0.20	N.F.I.	N.F.I.
	0.30	100000	100000
	0.40	100000	100000
	0.50	100000	100000
	0.70	100000	100000
LIGNOSOL XD	0.10	25.0	34.8
	0.20	22.5	19.3
	0.30	N.R.	N.R.
	0.40	12.6	17.6
	0.50	14.1	17.2

* N.F.I.: PITCH NOT FULLY INCORPORATED.
N.R.: NOT REDISPERSABLE.

Table 7.8 Viscosity as a function of surfactant concentration for slurries containing 50 wt% -200 mesh CANMET hydrocracked pitch (CONTINUED).

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	$9.3\ S^{-1}$ cP	$93\ S^{-1}$ cP
LIGNOSOL TSD	0.10	23.8	30.8
	0.20	21.9	17.4
	0.30	12.6	15.5
	0.40	13.8	17.8
MARASPERSE CBX-2	0.10	23.8	27.5
	0.20	13.8	17.8
	0.30	N.R.	N.R.
	0.40	N.R.	N.R.
MARASPERSE CBOS-3	0.10	N.F.I.	N.F.I.
	0.20	13.8	14.8
	0.30	N.R.	N.R.
	0.40	N.R.	N.R.
LIGNOSOL BD	INSUFFICIENT PITCH		

* N.F.I.: PITCH NOT FULLY INCORPORATED.
N.R.: NOT REDISPERSABLE.

Table 7.9 Viscosity as a function of surfactant concentration for slurries containing 60 wt% -200 mesh CANMET hydrocracked pitch.

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	9.3 S^{-1} cP	93 S^{-1} cP
PLURONIC F-108	0.10-0.90	N.F.I.	N.F.I
	1.80	N.F.I.	N.F.I.
	1.90	100000	100000
	2.00	100.0	318.0
	2.10	100000	100000
TETRONIC 1508	0.80-1.00	N.F.I.	N.F.I
	1.80	N.F.I.	N.F.I.
	1.90	13.8	10.5
	2.00	370.0	187.5
	2.10	15.3	10.3
ANTAROX DM-970	1.80	N.F.I.	N.F.I.
	1.90	N.F.I.	N.F.I.
	2.00	N.F.I.	N.F.I.
	2.20	N.F.I.	N.F.I.
	2.60	N.F.I.	N.F.I.
	3.00	N.F.I.	N.F.I.
LOMAR D	0.70	100000	100000
	0.80	20.0	16.4
	0.90	N.R.	N.R.
	1.00	N.R.	N.R.
FENOPON TK-32	1.80	N.F.I	N.F.I.
	1.90	N.F.I.	N.F.I.
	2.00	N.F.I.	N.F.I.
	2.20	N.F.I.	N.F.I.
	2.60	N.F.I.	N.F.I.
	3.00	N.F.I.	N.F.I.
LIGNOSOL XD	0.70	100000	100000
	0.80	N.R.	N.R.
	0.90	54.0	29.6
	1.00	N.R.	N.R.

* N.F.I.: PITCH NOT FULLY INCORPORATED.
N.R.: NOT REDISPERSABLE.

Table 7.9 Viscosity as a function of surfactant concentration for slurries containing 60 wt% -200 mesh CANMET hydrocracked pitch (CONTINUED).

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	$9.3\ S^{-1}$ cP	$93\ S^{-1}$ cP
LIGNOSOL TSD	0.70	100000	100000
	0.80	100000	100000
	0.90	50.0	55.3
	1.00	90.0	132.5
	1.10	95.0	95.0
MARASPERSE CBX-2	0.70	100000	100000
	0.80	80.0	129.4
	0.90	77.5	123.3
	1.00	N.R.	N.R.
MARASPERSE CBOS-3	0.70	100000	100000
	0.80	13.8	13.8
	0.90	40.0	20.1
	1.00	N.R.	N.R.
LIGNOSOL BD	INSUFFICIENT PITCH		

* N.F.I.: PITCH NOT FULLY INCORPORATED.
N.R.: NOT REDISPERSABLE.

usually more effective, at lower concentrations than were any of the other surfactants. The anionic surfactant, LOMAR D, was almost as effective as the lignosulphonates and more effective than any of the nonionic surfactants.

It is clear from the data in tables 7.8 and 7.9 that much more surfactant is required to significantly reduce the viscosities of slurries containing 60 wt% -200 mesh pitch than was required to achieve the same effect in slurries containing 50 wt% -200 mesh pitch. LOMAR D and the lignosulphonates significantly reduced the viscosities of slurries containing 60 wt% -200 mesh pitch when present in concentrations that were less than half that required by the most effective nonionic surfactants (PLURONIC F-108 and TETRONIC 1508). Neither ANTAROX DM-970 nor FENOPON TK-32 were effective at concentrations as high as 3.0 wt%.

It is evident from the data in table 7.7 that pseudoplastic (shear thinning) behavior was exhibited by almost every slurry containing 50 wt% -325 mesh pitch. Pseudoplastic behavior is very desirable since it provides high viscosity under low shear conditions, such as those experienced by settling particles, and low viscosity under high shear conditions such as those encountered during pumping. It can be attributed to the progressive destruction of loose aggregates of particles with increasing shear rate. The data in tables 7.8 and 7.9 indicate that many of the slurries containing -200 mesh pitch exhibit dilatant (shear thickening) behavior. Such behavior is not desirable for good slurry performance under high shear conditions such as pumping or atomization.

The data contained in tables 7.7 and 7.8 indicate that in most cases more surfactant is required to reduce the viscosity of a slurry containing 50 wt% -325 mesh pitch to a given value than is required to achieve the same effect in a slurry containing 50 wt% -200 mesh pitch. This would be expected if there was a greater degree of flocculation in the slurry containing smaller particles. It is likely that more surfactant is required to cover the larger total surface area of the smaller particles and thereby inhibit flocculation than would be required with larger particles.

7.6 Relationship Between A_{adj} And Slurry Rheology

Examination of the data in tables 7.1, 7.2, 7.3, 7.7, 7.8 and 7.9 indicate that there is little correlation between the value of A_{adj} and the viscosity of a slurry at 9.3 or 93 S^{-1}. However, more data are required before a relationship can be ruled out.

8.0 EVALUATION OF PETRO-CANADA HYDROCRACKED PITCH SLURRIES

8.1 Evaluation Of Mechanically Dispersed Slurries

8.1.1 Effect Of Surfactants On Slurry Behavior

8.1.1.1 Objective

Slurries were prepared containing 60 wt% PETRO-CANADA hydrocracked pitch and at least 8 concentrations of each surfactant in order to characterize the effect of surfactant concentration and type on slurry behavior. A further goal of this work was the determination of the optimum concentration of each surfactant (see section 7.1). Rod penetrometer test data obtained for these slurries were analyzed according to the method outlined in section 7.1. In this way, values of A_{adj} were obtained for each slurry that was tested. These values were used to evaluate the influence of the above mentioned parameters on the behavior of the slurries.

8.1.1.2 Effect Of Surfactant Concentration On Sediment Consistency

Figure 8.1 shows a typical plot of A_{adj} as a function of surfactant concentration for an effective surfactant (LIGNOSOL TSD). Such behavior is characterized by a reduction of A_{adj} to very low values ($\leq$ 5 g), at a surfactant concentration below 3.0 wt%. A_{adj} values of this magnitude are associated with excellent fluidity and the formation of small amounts of soft, easily redispersable sediment.

A_{adj} displays a minimum and then increases as the surfactant concentration is increased. This behavior is similar to that observed for slurries containing CANMET hydrocracked pitch and for oil sands coke slurries (148). However, the minima exhibited for slurries containing PETRO-CANADA hydrocracked pitch are much broader. The reasons for this difference are not clear.

As in the case of the CANMET hydrocracked pitch slurries, it is likely that the concentration dependence of A_{adj} can be attributed to a reduction in the extent of flocculation in the system with increasing surfactant concentration. Initially, the system is highly flocculated and resistance to sedimentation is extremely high. However, resistance to flow is also extremely high. As the degree of flocculation is reduced, a point is reached where the stabilizing influence provided by flocculation is just sufficient to prevent sedimentation without adversely affecting fluidity. The slurry exhibits the optimum concentration of stability and fluidity and the minimum value of A_{adj} at this point. The surfactant concentration at this point is called the optimum surfactant concentration (see section 7.1). When the surfactant concentration is increased beyond this point the stabilizing influence conferred by flocculation is increasingly reduced. This leads to increasing sedimentation and increasingly compact sediments.

Normally the surfactant concentration corresponding to the minimum value of A_{adj} represents the optimum concentrations of surfactant. In view of the breadth of the minima obtained for the PETRO-CANADA hydrocracked pitch slurries, it is necessary to define an optimum range of surfactant concentrations. Thus, a means for defining the bounds of this range is required. Ideally, such a limit would correspond to the minimum and maximum concentrations of surfactant that yielded an A_{adj} value of 0 g. However, very few slurries would meet such a criterion. Moreover, slurries which yield A_{adj} values of 5 g and less all exhibit acceptable slurry behavior. Consequently, the minimum and maximum concentrations of surfactant that yielded a value of 5 g for A_{adj} were selected as limits for the optimum range of surfactant concentrations.

Such limits were determined by assuming a linear dependence of A_{adj} on surfactant concentration between any two adjacent data points and determining the minimum and maximum surfactant concentrations that produce and A_{adj} value of 5 g. The optimum concentration range for LIGNOSOL TSD, determined on this basis, is shown in figure 8.1. Values of the optimum concentration range for each surfactant examined in this work are listed in Table 8.1.

8.1.1.3 Effect Of Varying Surfactant On Sediment Consistency

The optimum concentration ranges listed in Table 8.1 provide a means for evaluating the performance of each of the surfactants examined in this section. The most significant factor for this purpose is the optimum range lower limit (ORLL). The ORLL represents the lowest concentration of a given surfactant that can be used to obtain a slurry with an acceptable

Figure 8.1 A_{adj} as a function of surfactant concentration for slurries containing LIGNOSOL TSD and 60 wt% PETRO-CANADA hydrocracked pitch.

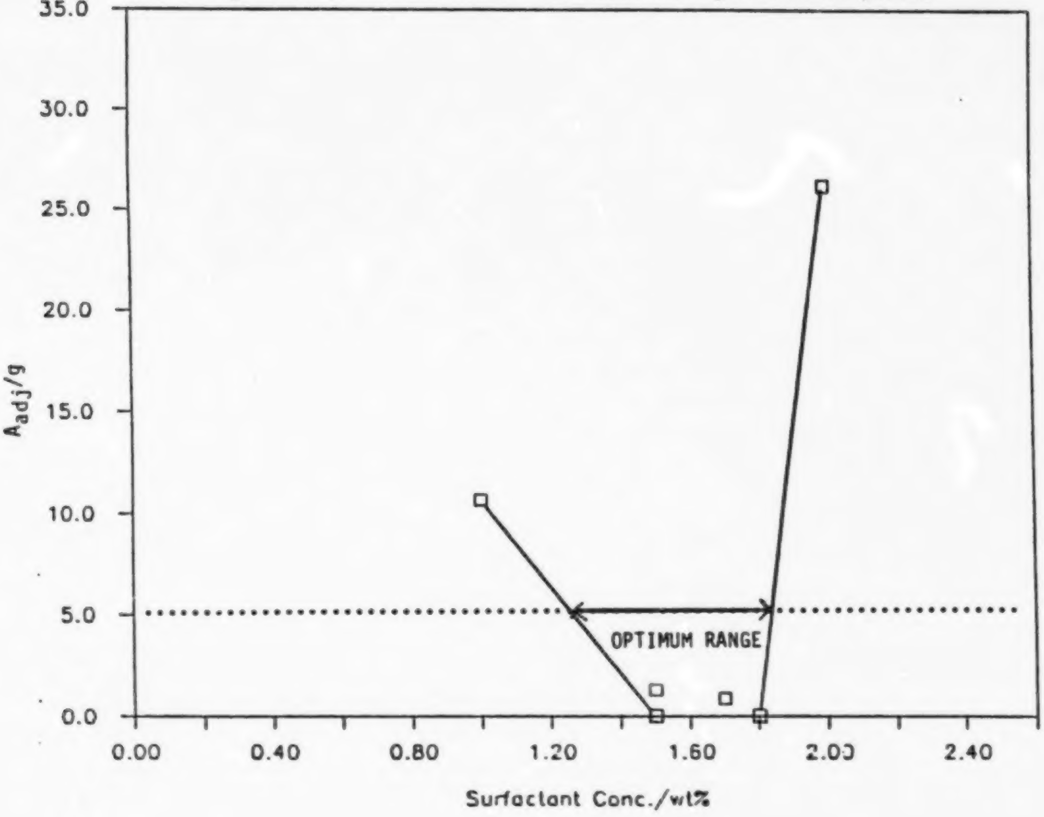


Table 8.1 Optimum surfactant concentration range for various surfactants in slurries containing 60 wt% PETRO-CANADA hydrocracked pitch.

SURFACTANT	OPTIMUM RANGE		SURFACTANT EFFECTIVENESS
	LOWER LIMIT wt%	UPPER LIMIT wt%	
LIGNOSOL XD	1.05	2.30	effective
LIGNOSOL BD	1.95	3.00	effective
LIGNOSOL TSD	1.25	1.85	effective
MARASPERSE CBX-2	3.00	--	ineffective
MARASPERSE CBOS-3	3.00	--	ineffective
LOMAR D	2.00	3.00	effective
PLURONIC F-108	3.50	3.70	ineffective
ANTAROX DM-730*	3.00	--	ineffective
ANTAROX DM-970*	3.00	--	ineffective
TETRONIC 1508*	3.00	--	ineffective
MASIL 2133*	3.00	--	ineffective

* pitch was not fully incorporated.

combination of fluidity and static stability and therefore is measure of the effectiveness of that surfactant. A more effective surfactant would be expected to give a lower ORLL.

On this basis, the lignosulphonate LIGNOSOL XD is the most effective of the surfactants examined in this work. The other LIGNOSOL brand lignosulphonates and the anionic surfactant LOMAR D were also very effective. Furthermore, it is evident from the data contained in Table 8.1 that the nonionic surfactants (PLURONIC F-108, ANTAROX DM-730, ANTAROX DM-970, TETRONIC 1508 and MASIL 2133) were not effective. In fact it was only possible to produce a slurry in which the pitch was fully incorporated with PLURONIC F-108 when concentrations in excess of 3.0 wt% were employed.

With the exception of the MARASPERSE brand lignosulphonates, it is clear that anionic surfactants are much more effective than the nonionic surfactants. These observations are in qualitative agreement with those recorded earlier for slurries containing CANMET hydrocracked pitch.

8.1.1.4 Slurry Rheology

It was previously noted that the presence of most surfactants caused the viscosities of CANMET hydrocracked pitch slurries to decline dramatically. After the large initial reduction, increasing the surfactant concentration had little effect on the slurry viscosity. The viscosities (at 9.3 and 93 S^{-1}) of slurries containing 60 wt% PETRO-CANADA hydrocracked pitch and various surfactants are given in Table 8.2. Although it is not indicated by the data contained in this table, behavior similar to that observed for the slurries containing CANMET hydrocracked pitch was observed. More specifically, the presence of the LIGNOSOL and MARASPERSE brand lignosulphonates and the LOMAR D surfactant greatly reduced the viscosities of slurries containing PETRO-CANADA hydrocracked pitch. It is clear that once the viscosities of the slurries had reached a level between approximately 150 and 500 cP, changing the concentration of surfactant had relatively little effect. Such behavior can be attributed to the reduction of particle flocculation in the presence of a surfactant.

It is evident from the data contained in Table 8.2 that LOMAR D was the most effective surfactant for slurry viscosity reduction. The viscosities of slurries prepared with this surfactant were generally 50 % lower than the most effective lignosulphonates (LIGNOSOL XD, LIGNOSOL TSD, MARASPERSE CBX-2 and MARASPERSE CBOS-3). LIGNOSOL BD was the least effective lignosulphonate for the reduction of slurry viscosity. This likely results from the calcium cation present in this surfactant since multivalent ions are known to enhance flocculation.

In general, except for PLURONIC F-108, the nonionic surfactants had little

Table 8.2 Viscosity as a function of surfactant concentration for slurries containing 60 wt% PETRO-CANADA hydrocracked pitch.

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	$9.3\ S^{-1}$ cP	$93\ S^{-1}$ cP
LOMAR D	0.80	161	208
	1.00	163	215
	1.20	119	128
	1.50	167	189
	1.80	117	93
	2.00	159	134
	2.50	153	102
	3.00	164	96
LIGNOSOL XD	1.00	352	427
	1.10	207	314
	1.20	222	403
	1.50	209	348
	2.00	164	312
	2.20	202	293
	2.30	181	273
	2.50	216	339
	3.00	222	357
LIGNOSOL TSD	1.00	293	427
	1.50	239	371
	1.70	185	266
	1.80	287	442
	2.00	227	354
	2.50	245	363
	2.90	222	270
	3.00	256	362

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 8.2 Viscosity as a function of surfactant concentration for slurries containing 60 wt% PETRO-CANADA hydrocracked pitch (CONTINUED).

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	9.3 S^{-1} cP	93 S^{-1} cP
LIGNOSOL BD	1.10	348	399
	1.40	416	500
	1.70	505	500
	1.90	481	500
	2.20	396	389
	2.50	488	477
	2.70	451	469
	3.00	542	440
MARASPERSE CBX-2	0.80	369	423
	1.00	214	376
	1.20	175	243
	1.50	216	295
	2.00	182	224
	2.20	244	284
	2.50	249	280
	2.70	176	184
	3.00	187	190
MARASPERSE CBOS-3	0.90	336	413
	1.00	318	432
	1.20	333	422
	1.50	229	339
	1.70	176	254
	2.20	187	245
	2.50	221	277
	2.70	261	340
PLURONIC F-108	1.00	145	181
	1.50	275	323
	1.80	248	269
	2.00	172	158
	2.80	276	257
	2.90	594	500
	3.00	287	247
	3.10	550	493
	3.20	728	500
	3.50	356	277
	3.70	548	500

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 8.2 Viscosity as a function of surfactant concentration for slurries containing 60 wt% PETRO-CANADA hydrocracked pitch (CONTINUED).

SURFACTANT		VISCOSITY*	
NAME	CONC. wt%	9.3 S^{-1} cP	93 S^{-1} cP
ANTAROX DM-930	0.10-3.00	N.F.I.	N.F.I.
ANTAROX DM-970	0.10-3.00	N.F.I.	N.F.I.
MASIL 2133	0.10-3.00	N.F.I.	N.F.I.
TETRONIC 1508	0.10-3.00	N.F.I.	N.F.I

* N.F.I.: PITCH NOT FULLY INCORPORATED.

effect on the viscosities of these slurries. Furthermore, results obtained for slurries containing concentrations of PLURONIC F-108 below 3.0 wt% may be artificially low. It was noted that several slurries containing PETRO-CANADA hydrocracked pitch and PLURONIC F-108 that were so viscous they that would not flow, became quite fluid after the prolonged low shear mixing which was used to redisperse the slurries prior to the viscosity measurements. This phenomenon was unique to slurries that contained PLURONIC F-108.

It is possible that when the slurries were first prepared, they were very dilatant. Thus, high shear mixing would not be efficient. Consequently, much of the pitch may not have been thoroughly mixed with the surfactant. Prolonged low shear mixing may allow more efficient mixing of the pitch with the surfactant which would yield a slurry with much lower viscosity. Although it is interesting, a thorough investigation of this behavior was beyond the scope of this work.

It is clear from the data in Table 8.2 that only slurries containing concentrations of LOMAR D in excess of 1.50 wt% and PLURONIC F-108 in excess of 3.00 wt% show pseudoplastic behavior. All of the other slurries exhibited dilatant behavior. Such behavior is not desirable for slurries that will be subjected to high shear conditions. On the basis of the data contained in Table 8.2, it is clear that LOMAR D yields slurries with the most desirable rheological properties.

8.1.2 Effect Of Pitch Concentration On Slurry Behavior

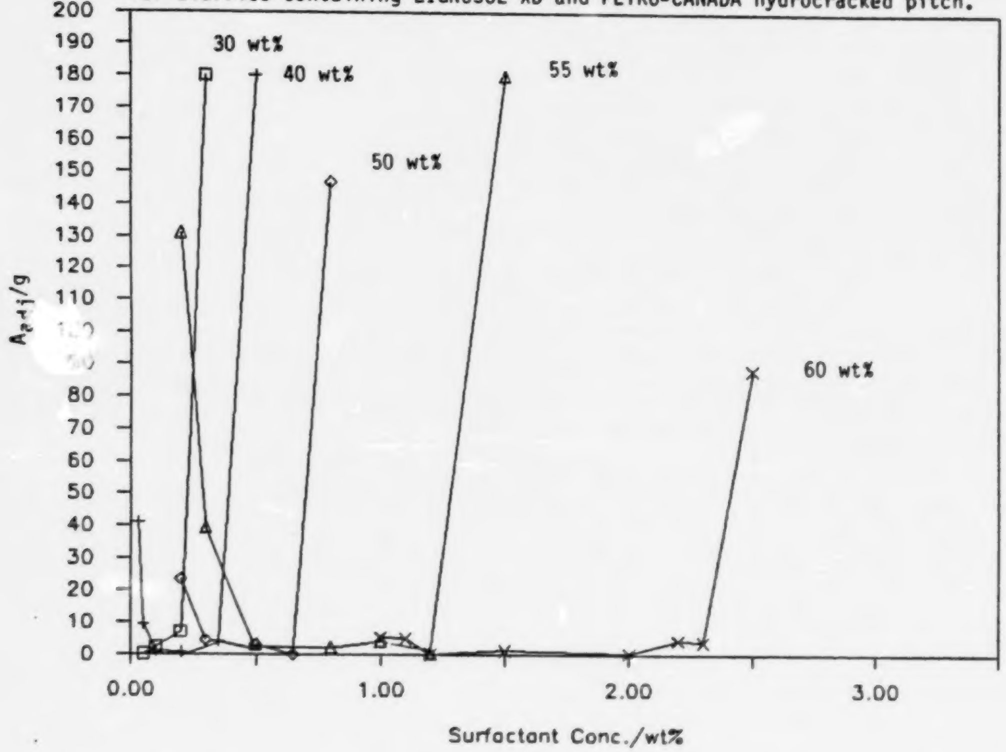
8.1.2.1 Effect Of Pitch Concentration On Surfactant Requirements

Slurries containing 30, 40, 50, 55, 60, 62, 65, and 70 wt% of PETRO-CANADA hydrocracked pitch and LIGNOSOL XD were prepared to evaluate the effect of pitch concentration, on the amount surfactant required to achieve a fluid but stable slurry. A plot of A_{adj} as a function of surfactant concentration for slurries containing 30 to 60 wt% is shown in figure 8.2. It was not possible to prepare slurries containing more than 62 wt% pitch or fluid slurries containing more than 60 wt% - even when surfactant concentrations as high as 7.0 wt% were employed. Thus, 60 wt% is the practical maximum concentration of PETRO-CANADA hydrocracked pitch that can be incorporated in slurries while maintaining desirable slurry behavior.

It is evident from figure 8.2, that the optimum range of stability shifts to higher concentrations as the pitch concentration increases. The nature of this shift can best be elucidated by examining the dependence of the limits of the optimum concentration range. The dependence of the ORLL (see section 8.1.1.3) on the pitch concentration is of particular interest since it represents the minimum surfactant concentration that will yield a slurry that exhibits the optimum combination of stability and fluidity.

Figure 8.3 shows values of the ORLL as a function of pitch

Figure 8.2 A_{adj} as a fuction of pitch concentration and surfactant concentration for slurries containing LIGNOSOL XD and PETRO-CANADA hydrocracked pitch.



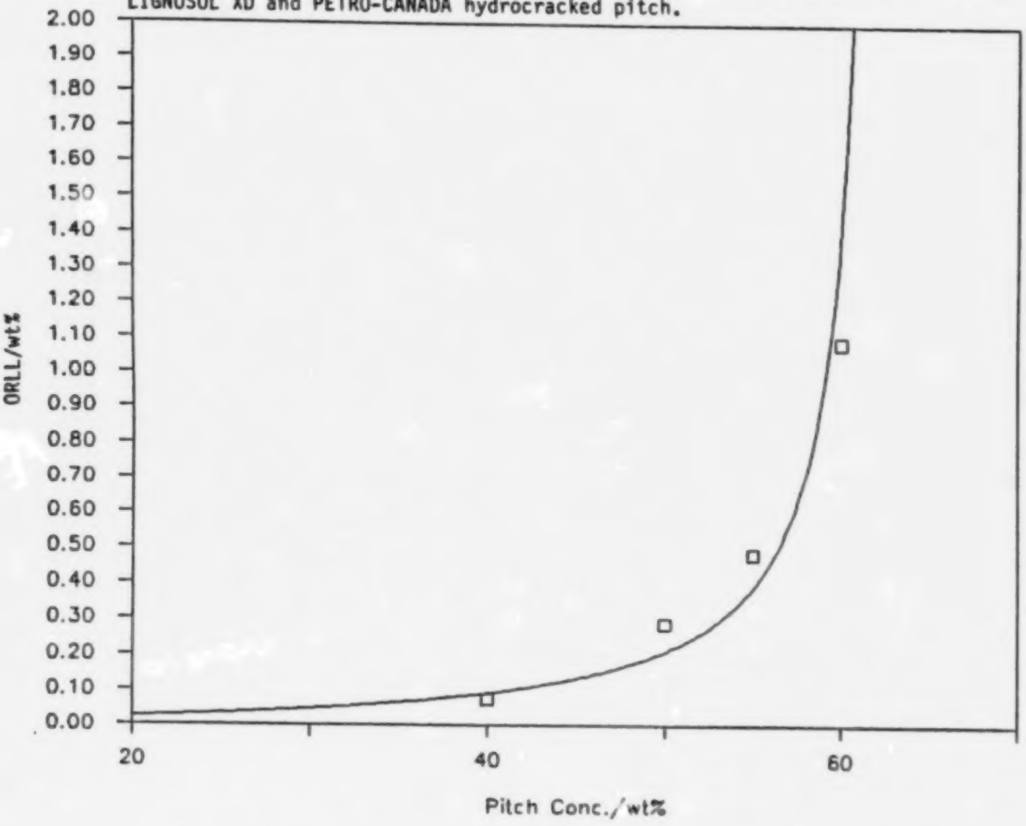
concentration (X). The form of this plot suggests that ORLL(X) can be described by a function of the form shown in equation [8.1].

$$\mathrm{ORLL} = \frac{BX}{(1 - X/X_{max})} \qquad [8.1]$$

where B is an empirical constant and X_{max} is the theoretical pitch concentration that yields an ORLL of infinity. Both parameters are probably highly dependent on: the PSD of the pitch, the chemical nature of the pitch and the particular surfactant that is employed. This type of function has been used to describe the dependence of several rheological properties on the solids concentration for concentrated suspensions (28,146,148,150,151). Such behavior is usually attributed to the approach of the solids concentration to the CVSC of the system (28,146,148,150,151). It is likely that some of the factors that influence rheological properties as the concentration approaches the CVSC also influence the ORLL.

The solid line shown in figure 8.3 represents a least squares fit of the data to a function of the form shown in equation [8.1]. This fit yielded values of $(8.2 \pm 0.9) \times 10^{-4}$ wt% surfactant (wt% pitch)$^{-1}$ and 62 ± 16 wt% pitch for B and X_{max} respectively. The relatively large uncertainty associated with each parameter is largely a reflection of the limited amount of data that was available. In spite its large uncertainty, the value obtained for X_{max} indicates that the pitch

Figure 8.3 ORLL as a function of pitch concentration for slurries containing LIGNOSOL XD and PETRO-CANADA hydrocracked pitch.



concentration must be below about 62 wt% if the slurry is to exhibit optimum behavior. Consequently, it is not surprising that it was not possible to prepare such slurries with pitch concentrations in excess of 60 wt%.

8.1.2.2 Effect Of Pitch Concentration On Slurry Rheology

The viscosities (at 9.3 and 93 S^{-1}) of slurries containing LIGNOSOL XD and PETRO-CANADA hydrocracked pitch are given as a function of pitch and surfactant concentration in Table 8.3. It is clear from this data that the concentration of surfactant that is required to significantly reduce the viscosity of a given slurry, increases dramatically with increasing pitch concentration. This is a reflection of the increased concentration of surfactant that is required to achieve a completely deflocculated system in a system with a higher pitch concentration. It is not unexpected that the concentration of surfactant required to achieve a given degree of dispersion (viscosity reduction) increases as the solids concentration increases since there are more inter-particle interactions to suppress.

The data contained in Table 8.3 also indicate that the minimum viscosity that is achieved, as a result of adding the surfactant, also increases dramatically with increasing pitch concentration. This is likely the result of the system's approach to the CVSC. It is well known that the viscosity of a dispersed system increases dramatically as the solids

Table 8.3 Viscosity as a function of surfactant concentration and pitch concentration for slurries containing PETRO-CANADA hydrocracked pitch and LIGNOSOL XD.

PITCH CONC. wt%	SURFACTANT CONC. wt%	VISCOSITY* $9.3\ S^{-1}$ cP	VISCOSITY* $93\ S^{-1}$ cP
30	0.05	22	8
	0.10	4	8
	0.20	6	3
	0.40	6	4
	0.60	8	4
40	0.03	784	289
	0.05	376	97
	0.10	41	20
	0.20	8	9
	0.35	7	8
	0.50	8	9
	0.80	9	8
50	0.10	1179	--
	0.20	396	153
	0.30	44	44
	0.40	32	41
	0.80	26	36
55	0.30	681	487
	0.50	115	178
	0.80	175	272
	1.00	132	235
	1.50	74	117
	2.00	72	109

* N.F.I.: PITCH NOT FULLY INCORPORATED.

Table 8.3 Viscosity as a function of surfactant concentration and pitch concentration for slurries containing PETRO-CANADA hydrocracked pitch and LIGNOSOL XD (CONTINUED).

PITCH CONC. wt%	SURFACTANT CONC. wt%	VISCOSITY* 9.3 S^{-1} cP	VISCOSITY* 93 S^{-1} cP
60	1.00	352	427
	1.10	207	314
	1.20	222	403
	1.50	209	348
	2.00	164	312
	2.20	202	293
	2.30	181	273
	2.50	216	339
	3.00	222	357
62	6.00	302	321
65	0-7.00	N.F.I.	N.F.I.
70	0-7.00	N.F.I.	N.F.I.

* N.F.I.: PITCH NOT FULLY INCORPORATED.

concentration approaches the CVSC (28).

8.2 Evaluation Of Ultrasonically Dispersed Slurries

None of the slurries that were prepared using intense ultrasound for mixing were completely dispersed. This became apparent after the slurries were stored for one week. During this period the slurry would separate into three distinct phases. A supernatant of varying turbidity and a small amount of sediment comprised two of these phases. Such phases were common to all slurries that were mechanically dispersed. However, the third phase was only observed for mechanically dispersed slurries that contained more than 62 wt% pitch.

The third phase was clearly composed of very small aggregates of pitch particles that were wet on the outside, but which contained substantial amounts of trapped air within them. Frequently, the bulk of the pitch was contained within this phase. This problem could be reduced by increasing the amount of time that the samples were exposed to the ultrasound but it could not be completely eliminated. These slurries would often appear to be quite fluid immediately after they were prepared since much of the pitch was not incorporated into the slurry. Thus, even meaningful qualitative observations were precluded.

Although several of these slurries would not have been completely dispersed by mechanical mixing; it is clear that intense ultrasound was much less effective as a means for dispersal of the pitch than was the mechanical mixer.

8.3 Relationship Between A_{adj} And Slurry Rheology

There seems to be little relationship between the value of A_{adj} and the viscosity of a slurry at 9.3 or 93 S^{-1}. Any relationship between A_{adj} and the slurry viscosity will be extremely complicated since A_{adj} depends primarily on the state of the slurry after 1 week while the viscosity can only be measured for a freshly dispersed slurry. It is likely that that the time dependence of the slurry viscosity is an important factor in determining the static stability of a slurry. Thus, a more sophisticated series of experiments would be required to define the nature of the relationship between A_{adj} and the slurry viscosity.

REFERENCES

(1) P.T. Ambrose and P.C. Flynn, Energy Processing/Canada, 46, Sept.-Oct., (1978).

(2) M.J. Rosen, Chemtech, 292, May, (1985).

(3) M.J. Rosen, **Surfactants** And Interfacial **Phenomena**, Wiley-Interscience, New York, 1978, Chapt. 1.

(4) W.M. Linfield ed., **A**nionic Surfactants **Part** I, Surfactant Science **Series, Vol**. 7, Marcel Dekker, New York, 1976.

(5) W.M. Linfield ed., Anionic **Surfactants Part** II, Surfactant Science **Series, Vol. 7**, Marcel Dekker, New York, 1976.

(6) E. Jungermann ed, **C**ationic Surfactants**,** Surfactant Science Series, **Vol. 4**, Marcel Dekker, New York, 1969.

(7) K. Shinoda ed., **S**olvent Properties Of Surfactants**,** Surfactant **Science Series, Vol. 2**, Marcel Dekker, New York, 1967.

(8) M.J. Schick ed, **N**onionic Surf**actants,** Surfactant Science Series, **Vol. 1**, Marcel Dekker, New York, 1967.

(9) T. Sato and R. Ruch, **Stabilization** Of Colloidal Dispersions By **Polymer Adsorption**, **Surfactant S**cience Series, Vol. **9**, Marcel Dekker, New York, 1980.

(10) M.J. Jacock and G.D. Parffitt, **C**hemistry **O**f Interfaces, Ellis-Horwood, Chichester U.K., 1981, Chapt. 5.

(11) A.W. Neumann, in **Wetting**, Spreading And **A**dhesion, J.F. Padday ed., Academic Press, New York, 1978, pp. 3-34.

(12) A.W. Neumann and R.J. Good, in **Surface** And **Colloid Science, V**ol. **11**, R.J. Good and R.R. Stromberg ed., Plenum Press, New York, 1979, Chapt. 2.

(13) L. Carino, Colloid Polym. Sci., **254**, 108, (1976).

(14) N.W.F. Kossen and P.M. Heertjes, Chem. Eng. Sci., **20**, 593, (1965).

(15) C.D. Parffitt and E.Z. Casaga, **Program** Of **Basic Research** On The **Utilization** Of **Coal-W**ater Mixture Fuels, Rept. DOE/PC/40285-10, (1984).

(16) P.J. Sell and P. Renzow, Prog. Org. Coatings, 3, 323, (1975).

(17) H.G. Bruil and J.J. Van Aartsen, Colloid Sci., **252**, 32, (1974).

(18) V.M. Rudoi, I.A. Okolova and V.A. Ogarev, Kolloidnyi Zhur., **45**, 1140, (1983).

(19) G.S. Contreras and J. Goldfarb, Colloid Sci., **256**, 241, (1978).

(20) R. Caggiano, D.D. Eley and M.J. Hey, Proc. Roy. Soc. London, **A**340, 176, (1974).

(21) R.J. Good and N.J. Lin, J. Colloid Interface Sci., **54**, 52, (1976).

(22) J. Szekely, A.W. Neumann and Y.K. Chuang, J. Colloid Interface Sci., **35**, 273, (1971).

(23) W.A. Zisman, **Contact Angle, Wettability** And Adhesion, Adv. In Chem. Ser., Vol. 43, A.C.S., Washington D.C., 1964, p.1.

(24) M.J. Rosen, **Surfactants And Interfacial Phenomena**, Wiley-Interscience, New York, 1978, Chapt. 9.

(25) T.F. Tadros, in **Surfactants**, T.F. Tadros ed., Academic Press, New York, 1984.

(26) E.L. Makor and J.H. Van der Waals, J. Colloid Sci., **7**, 775, (1952).

(27) E.J.W. Verwey and J.T. Ovverbeek, Theory **Of** The **Stability** Of **Lyophobic Colloids**, Elsevier, New York, (1948).

(28) T.C. Patton, **Paint Flow And Pigment Dispersion**, Wiley-Interscience, New York, (1979).

(29) S. Mark, Coal **Aqueous Slurries**, Preprints **Vol. 28**, Div. of Fuel Chem., Am. Chem. Soc., (1983).

(30) J.M.V. Blanshard and J.R. Mitchell, **Polysaccharides** In Food, Butterworths, London, (1979).

(31) S. Mark (Standard Oil Co.), US 4,478,603, 23 Oct. 1984.

(32) S. Mark (Gulf and Western Industries, Inc.), US 4,441,889, 10 Apr. 1984.

(33) S. Mark (Standard Oil Co.), US 4,488,881, 18 Dec. 1984.

(34) M.J. Schick and K.A. Knitter (Diamond Shamrock Corp.), US 4,415,338, 15 Nov. 1983.

(35) M.J. Schick and K.A. Knitter (Diamond Shamrock Corp.), US 4,436,528, 13 Mar. 1984.

(36) M. Iwako et al., **Proc. Fourth Int. Symp. On Coal Slurry Combustion And Technology**, May 10-12 1982, Orlando Fla., Pittsburg Energy Technology Center, Pittsburg Pa., (1982).

(37) Sanyo Chemical Industries Ltd., Jpn. Kokai Tokkyo Koho, JP 60,166,393, 29 Aug. 1985, in Chem. Abstr. **104**, no. 715988c.

(38) S. Nakai et. al., Kogakubu Kenkyu Hokoku, **36**, 227, (1986). in Chem. Abstr. **105**, no. 81923q.

(39) G.T. Colegrove and T.A. Lindroth (Merck and Co.), US 4,592,760, 22 Jan. 1985.

(40) G.L. Brode, J.P. Stanley and E.M. Partain (Union Carbide Corp.), US 4,579,942, 01 Apr. 1986.

(41) W.W. Howland et. al. (Henkel K.-G.a.A.), Eur. Pat. Appl., EP 186,164, 02 Jul. 1986.

(42) Babcock-Hitachi K.K., Jpn. Kokai Tokkyo koho, JP 61 60,788, 28 Mar. 1986, in Chem. Abstr. **105**, no. 9139w.

(43) P. Sherman, **Industrial Rheology**, Academic Press, New York, (1970).

(44) E.W. Sawyer (ITT Corp.), US 4,505,716, 19 Mar. 1985.

(45) R.W. Sparks and E.W. Sawyer, **Proc. Fourth Int. Symp. On Coal Slurry Combustion And Technology**, May 10-12 1982, Orlando Fla., Pittsburg Energy Technology Center, Pittsburg Pa., (1982).

(46) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 189,194, 26 Oct. 1984, in Chem Abstr., **102**, no. 152005t.

(47) Neos Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 199,794, 12 Nov. 1984, in Chem Abstr., 102, no. 169561u.

(48) Kao Corp., Nippon Oils And Fats Co., Ltd. and Lion Corp., Jpn. Kokai Tokkyo Koho, JP 59 204,690, 20 Nov. 1984, in Chem Abstr., 102, no. 187886h.

(49) G.R. Johnson et al (British Petroleum Co.), Eur. Pat. Appl., No. EP 125,592, 28 Nov. 1984, in Chem. Abstr., 102, no. 48605c.

(50) Nippon Oils And Fats Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 184,292, 28 Nov. 1984, in Chem Abstr., 102, no. 64811x.

(51) E.L. Kelley et al (Diamond Shamrock Chemicals Co.), US 4,478,602, 08 Jan. 1985, in Chem. Abstr., 102, no. 81469r.

(52) Electric Power Dev. Co., Ltd. and Kawasaki Heavy Idustries Ltd., Jpn. Kokai Tokkyo Koho, JP 59 179,696, 12 Oct. 1984, in Chem Abstr., **102**, no. 98237e.

(53) S. Mark (Diamond Shamrock Chemicals Co.), US 4,492,590, 06 Dec. 1982.

(54) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 174,693, 03 Oct. 1984, in Chem Abstr., **102**, no. 134857t.

(55) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 174,694, 03 Oct. 1984, in Chem Abstr., **102**, no. 134858t.

(56) R.N. Paul, B.K. Mall and M. Chakraborty (Council of Scientific and Induustrial Research (India)), IN 156,460, 10 Aug. 1985, in Chem. Abstr., **105**, no. 27021f.

(57) M. Carello and F. Rommanini (Agrip Petroi S.p.A.), Eur. Pat. Appl., EP 163,355, 29 May 1984.

(58) S. Maeda et al., **Proc. Seventh Int. Symp. On Coal Slurry Combustion And Technology**, May 21-24 1985, New Orleans La., Pittsburg Energy Technology Center, Pittsburg Pa.

(59) Kao Corp., Jpn. Kokai Tokkyo Koho, JP 59 145,293, 20 Aug. 1984, in Chem Abstr., 102, no. 64788v.

(60) Nippon Oils And Fats Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 120,232, 11 Jul. 1984, in Chem Abstr., 102, no. 9522d.

(61) Kao Corp., Jpn. Kokai Tokkyo Koho, JP 59 100,194, 09 Jun. 1984, in Chem Abstr., 102, no. 28179d.

(62) Nippon Oils And Fats Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 120,234, 11 Jul. 1984, in Chem Abstr., 102, no. 28202r.

(63) Nippon Oils And Fats Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 120,233, 11 Jul. 1984, in Chem Abstr., 102, no. 28203s.

(64) J.G. Papalos and J.V. Sinka (Diamond Shamrock Chemicals Co.), US 4,514,189, 30 Apr. 1985.

(65) E.W. Sawyer (I.T.T. Corp.), US 4,505,716, 19 Mar. 1985.

(66) J.G. Papalos et al (Diamond Shamrock Chemicals Co.), US 4,457,762, 03 Jul. 1984.

(67) M.J. Schick and K.A. Knitter (Diamond Shamrock Chemicals Co.), US 4,436,528, 13 Mar. 1984.

(68) A.W. Marcellis et al (Diamond Shamrock Chemicals Co.), US 4,501,594, 26 Feb. 1985.

(69) M.J. Schick and K.A. Knitter (Diamond Shamrock Chemicals Co.), US 4,415,338, 15 Nov. 1983.

(70) M.J. Schick and K.A. Knitter (Diamond Shamrock Chemicals Co.), US 4,492,589, 09 Jan. 1985.

(71) J.E. Funk (Alfred Univ. Research Foundation ,Inc.), US 4,468,232, 28 Aug. 1984.

(72) J.E. Funk (Alfred Univ. Research Foundation ,Inc.), US 4,441,887, 10 Apr. 1984.

(73) J.E. Funk (Alfred Univ. Research Foundation ,Inc.), US 4,477,259, 16 Oct. 1984.

(74) J.E. Funk (Alfred Univ. Research Foundation ,Inc.), US 4,479,806, 30 Oct. 1984.

(75) S. Mark (Standard Oil Co.), US 4,488,881, 18 Dec. 1984.

(76) S. Mark (Standard Oil Co.), US 4,358,293, 15 Nov. 1982.

(77) S. Mark (Gulf And Western Industries Inc.), US 4,441,889, 10 Apr. 1984.

(78) S. Mark (Standard Oil Co.), US 4,478,603, 23 Oct. 1984.

(79) L. Palumbo et al (Centro Sperimentale Metallurgico), Eur. Pat. Appl., EP 124,488, 07 Nov. 1984.

(80) Nippon Oils and Fats Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 61 183,390, 16 Aug. 1986, in Chem. Abstr., **106**, no. 7362k.

(81) K. Oppenlaender et. al. (B.A.S.F. A.-G.), Ger. Offen. DE 3,435,945, 03 Apr. 1986, in Chem. Abstr., **105**, no. 46168a.

(82) Babcock-Hitachi K.K., Jpn. Kokai Tokkyo Koho, JP 61 81,488, 25 Apr. 1986, in Chem. Abstr., **105**, no. 46170v.

(83) A. Feugier et. al. (Institut Francais du Petrole), Fr. Demande FR 2,567,902, 24 Jan 1986, in Chem. Abstr., **105**, no. 27020e.

(84) Sanyo Chemical Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 225,297, 07 Oct. 1986, in Chem. Abstr., **106**, no. 7380q.

(85) Babcock-Hitachi K.K., Jpn. Kokai Tokkyo Koho, JP 61 57,689, 24 Mar. 1986, in Chem. Abstr., **105**, no. 9144u.

(86) F. Yaghmate and R.J. McKeon (Texaco Development Corp.), Eur. Pat. Appl., EP 191,964, 27 Aug. 1986.

(87) Japan Synthetic Rubber Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 61 97,391, 15 May 1986, in Chem. Abstr., **105**, no. 156069b.

(88) Hitachi ltd., Babcock-Hitachi K.K., Jpn. Kokai Tokkyo Koho, JP 61 57,687, 24 Mar. 1986, in Chem. Abstr., **105**, no. 27023h.

(89) Kubota, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 225,289, 07 Oct. 1986, in Chem. Abstr., **106**, no. 7368s.

(90) Neos Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 61 223,093, 03 Oct. 1986, in Chem. Abstr., **106**, no. 7377u.

(91) Sanyo Chemical Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 225,298, 07 Oct. 1986, in Chem. Abstr., **106**, no. 7378v.

(92) Mitsubishi Heavy Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 250,096, 10 Dec. 1985, in Chem. Abstr., **105**, no. 27017j.

(93) K. Oppenlaender et. al. (B.A.S.F. A.-G.), Ger. Offen. DE 3,426,395, 23 Jan. 1986, in Chem. Abstr., **105**, no. 46166y.

(94) Kawasaki Steel Corp., Jpn. Kokai Tokkyo Koho, JP 61 164,142, 24 Jul. 1986, in Chem. Abstr., **105**, no. 175776w.

(95) Japan Synthetic Rubber Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 61 152,796, 11 Jul. 1986, in Chem. Abstr., **105**, no. 175770q.

(96) Babcock-Hitachi K.K., Jpn. Kokai Tokkyo Koho, JP 61 166,888, 28 Jul. 1986, in Chem. Abstr., **105**, no. 175771r.

(97) Lion Corp., Jpn. Kokai Tokkyo Koho, JP 61 176,697, 08 Aug. 1986, in Chem. Abstr., **105**, no. 175777x.

(98) J. Forand and J.A. Hellyer (Proctor and Gamble Co.), US 4,597,770, 01 Jul. 1986.

(99) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 61 188,494, 25 Sep. 1985, in Chem. Abstr., **105**, no. 136915w.

(100) Mitsubishi Heavy Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 130,395, 18 Jun. 1986, in Chem. Abstr., **105**, no. 136919a.

(101) Mitsubishi Heavy Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 130,396, 18 Jun. 1986, in Chem. Abstr., **105**, no. 136920u.

(102) P. Dilling (Westvaco Corp.), Ger. Offen. DE 3,535,565, 26 Jun. 1986, in Chem. Abstr., **105**, no. 116881d.

(103) Babcock-Hitachi K.K., Jpn. Kokai Tokkyo Koho, JP 61 141,791, 28 Jun. 1986, in Chem. Abstr., **105**, no. 136923x.

(104) Mitsubishi Heavy Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 143,493, 01 Jul. 1986, in Chem. Abstr., **105**, no. 136924y.

(105) K. Nakaoji et. al. (Electric Power Development Co., Ltd. and Sumitomo Heavy Industries, Ltd.), CA 1,207,923, 15 Jul 1986.

(106) Kubota, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 85,491, 01 May 1986, in Chem. Abstr., **105**, no. 100295e.

(107) Kubota, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 91,295, 09 May 1986, in Chem. Abstr., **105**, no. 100298h.

(108) Mitsubishi Heavy Industries, Ltd., Jpn. Kokai Tokkyo Koho, JP 61 98,795, 17 May 1986, in Chem. Abstr., **105**, no. 100299j.

(109) L. Jiang et. al. (Academia Sinica, Institute of Sensitization Chemistry), Faming Zhuanli Shenqing Gongkai Shuomingshu, CN 85,100,543, 20 Dec. 1985, in Chem. Abstr., **105**, no. 100300c.

(110) A. Naka et. al., Nenryo Kyokaishi, **64**, 213, (1985), in Chem. Abstr., **105**, no. 117810s.

(111) A. Naka et. al., Nippon Kagaku Kaishi, **10**, 1342, (1986), in Chem. Abstr., **105**, no. 229570v.

(112) M. Yamura et al,**Proc. Fourth Int. Symp. On Coal Slurry Combustion And Technology**, June 25-27, (1982), Orlando Fla., Pittsburg Energy Technology Center, Pittsburg Pa., (1982).

(113) Neos Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 179,139, 11 Oct. 1984, in Chem Abstr., **102**, no. 81568r.

(114) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 96,196, 24 Nov. 1982, in Chem Abstr., **102**, no. 28178r.

(115) Nippon Shokubai Kagaku Kogyo Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 58 213,094, 04 Jun. 1982, in Chem. Abstr., **102**, no. 25958k.

(116) Nippon Oils And Fats Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 187,090, 24 Oct. 1984, in Chem Abstr., 102, no. 64812y.

(117) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 60 26,091, 08 Feb. 1985, in Chem Abstr., 102, no. 206458p.

(118) Daiichi Kogyo Seiyaku Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 60 26,090, 08 Feb. 1985, in Chem Abstr., **102**, no. 206459q.

(119) J.E. Funk et al,**Proc. Fourth Int. Symp. On Coal Slurry Combustion And Technology**, June 25-27, 1982, Orlando Fla., Pittsburg Energy Technology Center, Pittsburg Pa. (1982).

(120) Mitsui Toatsu Chemicals, Inc. and Mitsui Mining Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 161,486, 12 Sep. 1984, in Chem. Abstr., **102**, no. 116482p.

(121) Mitsui Toatsu Chemicals, Inc. and Mitsui Mining Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 161,487, 12 Sep. 1984, in Chem. Abstr., **102**, no. 98233q.

(122) Chiyoda Chemical Engineering and Construction Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 60 206,898, 18 Oct. 1985, in Chem Abstr., **104**, no. 71587y.

(123) Nikka Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 206,896, 18 Oct. 1985, in Chem Abstr., **104**, no. 112677y.

(124) Chiyoda Chemical Engineering and Construction Co., Ltd. and Nikka Chemical Industry Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 59 206,863, 18 Oct. 1985, in Chem Abstr., **104**, no. 152195w.

(125) Japan Synthetic Rubber Co., Ltd., Jpn. Kokai Tokkyo Koho, JP 61 76,590, 19 Apr. 1986, in Chem. Abstr., **105**, no. 156070v.

(126) G.D. Vergazova et. al. (U.S.S.R.), SU 1,182,387, 30 Sep. 1985, in Chem. Abstr., **104**, no. 36813x.

(127) R.J. Corbeels and S.R. Vasconellos (Texaco Inc.), US 4,575,381, 11 Mar. 1986.

(128) H. Ljusberg-Wahren (Berguik Kemi Ab.), Eur. Pat. Appl., EP 131,558, 16 Jan. 1985.

(129) Canadian Waste Materials Exchange, Bull. No. 46, Sept. 1985.

(130) F. Yaghmaie and R.J. Mc Keon (Texaco Inc.), US 4,502,868, 05 Mar. 1985.

(131) P.L. Belkevich et. al., Khim. Tverd. Topl. (Moscow), 2, 73, (1986), in Chem. Abstr., **104**, no. 209849u.

(132) R.W. Whorlow, **Rheological Techniques**, John Wiley And Sons Canada Ltd., Toronto, (1980), Chapt. 1.

(133) J.R. Van Wazer et. al., **Viscosity and Flow Measurement-A Laboratory Handbook of Rheology.**, John Wiley And Sons Inc., New York, 1963, Chapt. 1.

(134) T. Dabak and O. Yucel, **Proc. Tenth Int. Conf. On Slurry Tech.**, March 26-28 1985, Lake Tahoe Nevada, Slurry Technology Association, Washington D.C., p. 265 (1985).

(135) S.C. Tsai and E.W. Knell, Fuel, **65**, 566, (1986).

(136) M.E. Morgan et. al., **Proc. Seventh Int. Symp. On Coal Slurry Combustion And Technology**, May 21-24 1985, New Orleans La., Pittsburg Energy Technology Center, Pittsburg Pa., p. 105, (1985).

(137) A.N. Hassan, D.N. Baria and A.V. Rao, Chem. Eng. Commun., **46**, 227, (1986).

(138) W.G. Rakitsky, E.G. Knell and T.J. Murphy, **Proc. Eleventh Int. Conf. On Slurry Tech.**, March 26-28 1986, Hilton Head, S.C., Slurry Technology Association, Washington D.C., p. 137 (1986).

(139) J.A. Williams, W.O. Akoto and C.C. Tagoe, **Proc. Seventh Int. Symp. On Coal Slurry Combustion And Technology**, May 21-24 1985, New Orleans La., Pittsburg Energy Technology Center, Pittsburg Pa., p. 155, (1985).

(140) O. Yucel and T. Dabak,**Proc. Seventh Int. Symp. On Coal Slurry Combustion And Technology**, May 21-24 1985, New Orleans La., Pittsburg Energy Technology Center, Pittsburg Pa., p. 91, (1985).

(141) E. Jimenez G., R.M. De Diego and M.M. Perez, **Proc. Eleventh Int. Conf. On Slurry Tech.**, March 26-28 1986, Hilton Head, S.C., Slurry Technology Association, Washington D.C., p. 89, (1986).

(142) H. Usui et. al., J. Chem. Eng. Japan, **17**, 583, (1984).

(143) J.K. Szymanski and N. Mansour, **Proc. Eleventh Int. Conf. On Slurry Tech.**, March 26-28 1986, Hilton Head, S.C., Slurry Technology Association, Washington D.C., p. 101, (1986).

(144) A. Naka et. al., Tenside Detergents, 23, 208, (1986).

(145) G.F. Round and A.R. Hessari, **Proc. Tenth Int. Conf. On Slurry Tech.**, March 26-28 1985, Lake Tahoe Nevada, Slurry Technology Association, Washington D.C., p. 151 (1985).

(146) T. Dabak and O. Yucel, **Proc. Eleventh Int. Conf. On Slurry Tech.**, March 26-28 1986, Hilton Head, S.C., Slurry Technology Association, Washington D.C., p. 81, (1986).

(147) P. Kruus and T.J. Patraboy, **Preparation Of Oil Sand Coke - Water Slurry For Entrained Bed Gasifier Using Ultrasonic Treatment. - Second Interim Report. Dec. 1, 1985 - Jan. 24, 1986**, Report CANMET Contract No. OST85-00169, Jan. (1986).

(148) P. Kruus and T.J. Patraboy, **Preparation Of Oil Sand Coke - Water Slurry For Entrained Bed Gasifier Using Ultrasonic Treatment. - Third Interim Report. Feb. 1, 1986 - June 1, 1986**, Report CANMET Contract No. OST85-00169, June (1986).

(149) P. Kruus and T.J. Patraboy, **Preparation Of Oil Sand Coke - Water Slurry For Entrained Bed Gasifier Using Ultrasonic Treatment. - First Quarter Report. Sept. 1, 1985 - Dec. 1, 1985**, Report CANMET Contract No. OST85-00169, Dec. (1986).

(150) D.I. Lee, J. Paint Tech., **42**, 1970, 579.

(151) E.C. Gay, P.A. Nelson and W.P. Armstrong, A.I.Ch.E. Journal, **15**, 1969, 815.